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# Evaluating the Impact of a Wood-chip Bioreactor on Phosphorus Concentrations

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EVALUATING THE IMPACT OF A WOOD-CHIP BIOREACTOR ON PHOSPHORUS CONCENTRATIONS

For the degree of Master of Science in Agricultural and Biological Engineering

Is approved by the final examining committee:

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Laura Bowling

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Date

EVALUATING THE IMPACT OF A WOOD-CHIP BIOREACTOR  
ON PHOSPHORUS CONCENTRATIONS

A Thesis

Submitted to the Faculty

of

Purdue University

by

Amanda M. Brock

In Partial Fulfillment of the

Requirements for the Degree

of

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## ABSTRACT

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Loss of nitrogen (N) and phosphorus (P) into rivers through subsurface tile drains causes eutrophication, which is a concern for aquatic ecosystems. Denitrifying bioreactors are shown to effectively reduce the losses of nitrate ( $\text{NO}_3$ ), however, little is known of their effects on P losses. A bioreactor at Throckmorton Purdue Agricultural Center (TPAC), located south of Lafayette, Indiana, has been shown to reduce  $\text{NO}_3$  concentrations of the effluent to approximately 0 mg N/L. However, an increase in the concentration of soluble reactive phosphorus (SRP) was observed in the bioreactor effluent during the monitoring period.

To evaluate the effects of a bioreactor on P losses, three lab-scale anaerobic water columns were constructed using the same wood-chips as those in the TPAC bioreactor. Results from the water column tests showed an increase in the SRP concentrations for all columns with varying rates of increase. The highest concentration was over 7 mg P/L. Fungal growth discovered on the wood-chips led to two subsequent tests to determine the effect of the growth on SRP losses. An aerobic degradation test was done using wood-chips from the water columns and a nitrate solution on a shaker table. Under aerobic conditions, SRP concentrations increased to a maximum of 1.2 mg P/L, after which they



leveled off and remained around 0.07 mg P/L. An anaerobic test was conducted using three replicates of non-sterilized wood-chips and three replicates of sterilized wood-chips. Results indicated that the sterilized wood-chips had slightly higher SRP concentration outputs than the non-sterilized wood-chips. However, the SRP concentrations between the two types of wood-chips did not vary significantly.

Bauxite residue pressed into disks and sintered was tested as a potential remediation for reducing SRP loss from the bioreactor effluent. Bauxite disks of varying pH and varying salt content were used for bench-top SRP sorption tests. The results indicated that the bauxite disks could reduce SRP concentrations by 70-100%. A one-hour P-test was conducted on one bauxite disk with 3% salt. The 3% salt disk was observed to reduce SRP concentrations by roughly 25%. A lab-scale version of a bioreactor outflow box was constructed to test the performance of the bauxite disks under scaled field operating conditions. Two bauxite disks with different percentages of salt were individually placed in the box and samples were taken from the effluent. For both disks, there was no noticeable change in the SRP concentration of the effluent. Because the observed influent of the bioreactor lab test has an SRP concentration of 0 mg P/L, it is hypothesized that the P concentration seen in the effluent originated from the wood-chips as they decomposed. This study indicates that the solid bauxite disks are capable of absorbing P from the overlying water column, but their performance decreased considerably under flowing water conditions.

## CHAPTER 1. INTRODUCTION

### 1.1 Agricultural Water Quality and Tile Drainage

Advancements in agricultural technology and farm management practices have helped to increase crop yields over the years, however, some of the agricultural management practices have unintended water quality impacts. Subsurface drainage systems made of perforated pipes (commonly known as subsurface tile drains) underlay fields, which allow water to move into them from the overlaying soil. The movement of water into the tile drains helps to lower the water table and keeps fields well drained for better growing conditions for crops. The water that moves through the tile drains is then directed towards the nearest water body, which typically is a ditch or a stream. Tile drains are ubiquitous in the Midwestern states having large agricultural areas dominated by poorly drained soils. Five of the Corn Belt states and three Great Lake states (Wisconsin, Illinois, Missouri, Iowa, Indiana, Ohio, Minnesota, and Michigan) were reported to have a total cropland area drained by subsurface tiles of 16 million hectares (28.7% of total cropland) (Sugg, 2007).

Agricultural water quality problems stem from the losses of nutrients applied as organic or inorganic fertilizers to support crop growth. For row crops grown in the Midwest, fields are typically fertilized at rates ranging from 100 to 200 kg N ha<sup>-1</sup> yr<sup>-1</sup>

with only 50% of the applied nitrogen contained in the crop grain yield (David et al., 1997). In a study done by the University of Illinois, a 40 ha watershed that was fertilized at a rate of  $135 \text{ kg N ha}^{-1}$  saw an export of  $29.2 \text{ kg N ha}^{-1}$  in 1995 and  $48.3 \text{ kg N ha}^{-1}$  in 1996 through tile drains with a range of 21.6 - 35.8% of the fertilizer applied lost to subsurface drainage (David et al., 1997). In Indiana, Kladvko et al. (2004) observed annual N losses from chisel plowed corn plots that ranged from 27 to  $50 \text{ kg ha}^{-1}$  over a 3-year period (1986-1988). The total N fertilizer applied to these fields was  $285 \text{ kg ha}^{-1} \text{ yr}^{-1}$  (Kladvko et al. 2004). Based on a simulation analysis, Ale (2009) reported similar N losses through tile drains from chisel plowed plots that had continuous corn and rotational corn-soybean. In this study, both the continuous corn and the corn-soybean plots were each split into three sections with each section designated as receiving either a low, medium, or high application of N fertilizer ( $157$ ,  $179$ , &  $202 \text{ kg-N ha}^{-1}$ ) (Ale, 2009). Over the seven-year simulation period, annual nitrate loads in tile drains totaled 98.3, 89.2, and  $119.1 \text{ kg ha}^{-1}$  (low, medium, and high application) for continuous corn and 123.9, 110.2, and  $136.8 \text{ kg ha}^{-1}$  for corn-soybean rotation (Ale, 2009). Excess amounts of nutrients lost to the receiving waterbodies can stimulate plant and algae growth resulting in eutrophication (USEPA, 2001).

## 1.2 Agricultural Conservation Practices

Both non-structural and structural agricultural conservation practices are recommended to reduce the losses of nutrients from agricultural fields. Non-structural conservation practices include fertilizer application rates and the timing of fertilizer application. Similarly, structural practices include cover crops and riparian buffer strips.

Better managing of fertilizer application can reduce the amount of nitrogen lost. Spring is the time when the risk of losing N is greatest, due to relatively large precipitation events that typically occur in late May and June (Scharf et al., 2006). Applying N fertilizer close to the crop's maximum growth period has a much lower risk of N loss as this is the time when a rapid uptake of N occurs in the crops (Scharf et al., 2006). Sidedressing the fertilizer also has the potential to lower the amount of loss occurring when compared to fall application. Jaynes (2015) compared nitrate concentrations coming from tile drainage over a four-year period between fall application and sidedressing of fertilizer on a field and saw that the average concentration from sidedressing was lower than that from fall application. Nitrate concentrations varied from 9.0 to 16.0 mg N L<sup>-1</sup> with an average of 11.8 mg N L<sup>-1</sup> for fall application while those for sidedressing varied from 6.8 to 13.8 mg N L<sup>-1</sup> with an average of 10.0 mg N L<sup>-1</sup> (Jaynes, 2015). The amount of N loss, however, depends on several factors including amount of precipitation and soil type (Scharf et al., 2006).

Cover crops can take up excess nitrogen present in the soil, and can potentially reduce losses of N to tile drains and ground water (Clark et al., 2007). Barley used as a cover crop was able to remove 64% of N in soil that had an average N application of 120

kg N ha<sup>-1</sup> (Jordan et al., 1994 cited in Clark et al., 2007). Similarly, Merriman et al. (2009) found that winter cover crops in Arkansas were able to reduce an average of 75% of nitrate losses. The uptake of nitrate is not the only way that cover crops can help improve water quality. Legume cover crops can convert atmospheric nitrogen gas into a form of nitrogen that crops can uptake in the subsequent years (Clark et al., 2007). Crops grown after the legumes have been shown to use at least 30-60% of the nitrogen fixed by the legumes, which could reduce the amount of fertilizer applied to the field (Clark et al., 2007).

Riparian buffer zones are also able to influence water quality as they can take up excess nutrients and other contaminants in runoff, but the percentage of these contaminants that they remove varies widely (Klapproth & Johnson, 2009). For example, one study in Maryland found that the nitrate concentration of groundwater decreased from 8 mg N/L to 0.4 mg N/L, (95% reduction) (Jordan et al., 1993) while another study in Richmond, Virginia reported a 48% reduction of nitrate by the riparian zone (Snyder et al., 1995 cited in Klapproth & Johnson, 2009). Riparian buffers, however, mainly filter sediment and nutrients from surface runoff. Since runoff from tile drains typically bypass riparian buffers, they are largely ineffective in tile-drained environments.

One conservation practice that has been shown to reduce N losses from tile-drained systems is drainage water management. Water control structures are incorporated into a tile drain to allow for variance in the depth at which drainage from the pipe can occur (Frankenberger et al., 2006). Water is held in the agricultural fields during the non-growing season allowing for denitrification to take place. Increased denitrification during

the non-growing period reduces N losses through tile drains. In Arkansas, drainage water management has been observed to reduce an average of 56% of nitrate (Merriman et al., 2009). Similarly, Ale et al. (2012) simulated a 46% reduction in nitrate losses through drainage water management in west central Indiana.

### 1.3 Agricultural Denitrifying Bioreactors

Infield anaerobic bioreactors are a practice that works in a tile-drained environment to reduce losses of nitrate to surface water. A bioreactor is a large trench or pit filled with a carbon material, typically wood-chips, which intercepts water from subsurface tile drains (Bell et al., 2015). There are three important features of a bioreactor: an inflow control box that routes water into the bioreactor, the bed of wood-chips interacts with the water and acts as a food source for microbes, and an outflow control box which can be manipulated to retain the water inside of the bioreactor (Christianson et al., 2011). The water is held in the bioreactor to allow for denitrification, a microbial process where nitrate-nitrogen ( $\text{NO}_3^-$ ) replaces  $\text{O}_2$  as an electron acceptor and in the process is reduced to nitrogen gas ( $\text{N}_2$ ) (Lassiter & Easton, 2013; Christianson et al., 2011).

Though research on bioreactors has shown their effectiveness to reduce nitrate from agricultural drainage water (Thompson et al., 2014; Lassiter & Easton, 2013; Wildman, 2001 cited in Christianson et al., 2012), their effectiveness on phosphorus is not as certain. Lassiter & Easton (2013) reported a decrease in the average soluble

reactive phosphorus (SRP) concentration from 0.36 mg P/L to 0.23 mg P/L from the bioreactor effluent. Bell et al. (2015) reported effluent SRP concentrations that were approximately 5 mg P/L higher than the influent concentrations for the first three events. However, no substantial difference between the influent and effluent concentrations was reported for the subsequent events (Bell et al., 2015). Chichlowski (2014) monitored effectiveness of a wood-chip bioreactor installed at the Throckmorton Purdue Agricultural Center in West Lafayette, Indiana for 17 flow events that occurred between 2013 and 2014. Over the course of a 17-month duration the average nitrate concentration was reduced from 9.4 mg N/L to 0.58 mg N/L. However, the average SRP concentration was increased from 0.02 mg P/L to 1.29 mg P/L during the same period (Chichlowski, 2014).

#### 1.4 Purpose of Study

The overall goal of this study is to evaluate the effects of a wood-chip bioreactor on phosphorus losses and test a possible remediation technique to further reduce P losses from the bioreactor. Specific objectives were to: (1) quantify phosphorus release from wood-chips using a lab-scale water column test and (2) determine if bauxite material can be used to lower the SRP concentration from a bioreactor effluent.

This study will show if the additional phosphorus coming out of the bioreactor is being released from the wood-chips and also determine expected SRP concentrations from a bioreactor under overlaying water conditions. This study will also determine

whether bauxite residue in a hardened form has the potential to be repurposed as a filter in a denitrifying bioreactor. Bauxite residue is currently a waste product with no use so repurposing it could open up new markets for its use in reducing phosphorus losses, including losses from bioreactor effluent. The thesis is organized as introduction and objectives of this study (this chapter), followed by a review of related published literature. Material and methods used in this study is described in Chapter 3. Results from various lab tests are discussed in Chapter 4 followed by overall conclusions and recommendations for future research in Chapter 5.



## CHAPTER 2. LITERATURE REVIEW

### 2.1 Phosphorus Cycle in Soil and Water

In soil, phosphorus can be found in both organic and inorganic forms, but the distribution depends on the soil type (Espinoza et al., 2005). Roughly 20-80% of the phosphorus in a typical surface soil is in the organic form, found in compounds such as phospholipids and nucleic acids, while the majority of the phosphorus in the soil solution is dissolved organic phosphorus (DOP), also called soluble reactive phosphorus (SRP) (Brady & Weil, 2010). Organic forms of phosphorus are typically not available for plant uptake, but P can be made available by microbial activity that will mineralize the P (Espinoza et al., 2005). Mineralization, however, is influenced by pH, temperature, moisture and the structure of the organic matter in the soil (Espinoza et al., 2005; Brady & Weil, 2010).

Inorganic phosphorus in soil is generally fixed by aluminum and iron in low pH soils and calcium compounds in high pH soils (Sylvia et al., 2005). These bound forms of inorganic phosphorus are unavailable for plant uptake, which is why in soil the greatest amount of plant available phosphorus can be found in soils around a neutral pH (Brady & Weil, 2010). The inorganic phosphorus compounds are also slightly soluble and can be released when compounds are exposed to water (Brady & Weil, 2010). Inorganic soluble

phosphorus can enter the roots of plants by diffusion (Sylvia et al., 2005), but if not taken up by the plants the phosphorus could either become fixed to soil particles or continue to move with the water in dissolved or particulate forms.

In agricultural settings, phosphorus enters into nearby water systems primarily through runoff. Sediment-attached and dissolved phosphorus are the two primary forms of phosphorus transported by runoff (Lory, 1999). Phosphorus can also leach to groundwater, but this is generally a small amount of the overall phosphorus lost (Brady & Weil, 2010). After entering a water system, the phosphorus will cycle between dissolved and sediment-attached forms until it is taken up by aquatic vegetation and algae (Lory, 1999).

## 2.2 Agricultural Conservation Practices to Regulate Phosphorus

Structural and non-structural agricultural conservation practices have been studied for their ability to reduce the loss of phosphorus from agricultural fields. Non-structural practices include using nutrient management planning and altering tillage type. Structural practices can consist of cover crops, changing fertilizer formulations, using riparian buffer zones and drainage water management. However, many of these practices have been found to affect particulate phosphorus over soluble reactive phosphorus (Gitau et al., 2005).

Nutrient management plans can help to reduce accumulation of phosphorus in soils or losses in runoff. Thompson et al. (2014) reported that using soil P tests before deciding

to apply P fertilizers and adjusting the fertilizer application rate accordingly can result in an average reduction of 17% of phosphorus load losses. When applying phosphorus fertilizer, Smith et al. (2016) observed that using polyammonium phosphate resulted in a phosphorus loss of 0.17%. In comparison, using poultry litter has been observed to have a relative phosphorus loss of 4.8% (Smith et al., 2016). Gitau et al. (2005) collected BMP effectiveness data from literature and found that overall, implementing a nutrient management plan can reduce an average of 47% of total phosphorus (TP), 46% of particulate phosphorus (PP), and 26% of SRP.

Changing from traditional tillage practices to no-till or conservation tillage practices has been reported to reduce the loss of phosphorus as well. Conservation tillage has been reported to reduce the loss of total phosphorus up to 62% (Thompson et al., 2014; Merriman et al., 2009; Gitau et al., 2005) with a 63% reduction of particulate phosphorus (PP) lost (Gitau et al., 2005). In comparison, the use of no-till practices has been reported to reduce the loss of total phosphorus by 69- 90% (Merriman et al., 2009; Czapar et al., 2005; Thompson et al., 2014) with a 60% reduction of PP and a 24% reduction in soluble phosphorus (Merriman et al., 2009). However, Shipitalo et al. (2013) reported that no-till watersheds had an average total dissolved phosphorus (TDP) loss of  $0.32 \text{ kg ha}^{-1} \text{ yr}^{-1}$  while chisel-till watersheds had an average TDP loss of  $0.21 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . Similarly, Lam et al. (2016) reported that SRP loads in the tile drains of a field under reduced tillage were greater than the SRP loads from the tiles draining an annually tilled field. Over a two-year period, Lam et al. (2016) reported loads of  $190 \text{ g SRP ha}^{-1}$  and  $13 \text{ g SRP ha}^{-1}$  in the reduced tillage plot for the years 2011 and 2012 respectively. The

annually tilled plot was reported to have SRP loads in the tiles of 18 g SRP ha<sup>-1</sup> and 5 g SRP ha<sup>-1</sup> for the years 2011 and 2012 respectively (Lam et al., 2016).

The use of cover crops can reduce phosphorus loss, but the amount reduced varies by plant type. Thompson et al. (2014) reported that winter rye can reduce phosphorus loss by 29%. Similarly, Merriman et al. (2009) reported that winter cover crops reduced the loss of DP in surface runoff by 37%. Zhu et al. (1989) evaluated the effectiveness of common chickweed (CW), Canadian bluegrass (CB) and Downy Brome (DB) for their ability to reduce phosphorus losses in surface runoff. Chickweed was reported to reduce phosphorus loss by 63%, bluegrass reduced the loss by 6.5% and Downy Brome reduced the loss by 41% (Zhu et al., 1989). Kaspar et al. (2008) reported that overall, reduction of TP losses in surface runoff by cover crops in their study ranged from 54% to 94% in the Upper Mississippi River Basin.

Another practice that has been found to reduce phosphorus losses are riparian buffer zones. Merriman et al. (2009) reported a greater than 50% reduction in different forms of phosphorus by riparian buffers. PP loss was reduced by 63% and TP was reduced by 53% with no reported effect on SRP (Merriman et al., 2009). Mankin et al. (2007) evaluated three possible compositions for a riparian buffer zone: a natural selection of grasses (NS), native grasses with American plum shrubs (NG/P) and a natural selection of grasses along with American plum shrubs (NS/P). Reductions in the mass of TP observed ranged from 84.6% - 96% over the three types of buffers with an overall average reduction of 91.8% (Mankin et al., 2007). Mankin et al. (2007) also

reported concentration reductions from 11% - 23% for DP and 35.1% - 53.1% for TP over the three types of buffers.

Recent studies have reported that a significant loss of phosphorus can occur through tile drains (King et al., 2014). Drainage control structures are one practice that has been researched for reducing the loss of phosphorus through tile drains. During the first year of the treatment period, Feset et al. (2010) reported that the annual TP load coming from the controlled drainage field was 77% lower than the TP load from a free-drainage field. During the same period, the soluble reactive phosphorus (SRP) load from the controlled drainage field was 75% lower than the SRP load from the free-drainage field (Feset et al., 2010). However, in the subsequent year they saw only a 25% reduction in annual TP load losses and there was no change for SRP loads, which seems to be due to a decrease in the annual loads from free-drainage between 2008-2009. From 2008-2009, free-drainage TP load decreased from 0.13 to 0.04 kg P/ha and SRP load decreased from 0.08 to 0.01 kg P/ha (Feset et al., 2010).

### 2.3 Phosphorus and Bioreactors

Edge of field bioreactors have been investigated for their ability to reduce the amount of nitrate from tile drains (Christianson et al., 2012). Many studies have reported that bioreactors are very effective in reducing the losses of nitrate-nitrogen, ranging from 20% to 98% (Bell et al., 2015). However, data related to their effects on phosphorus is sparse. Bell et al. (2015) reported that the concentrations of soluble reactive phosphorus

in the effluent from a wood-chip bioreactor were higher than those in the influent water. However, the authors reported that the P losses reduced with time where effluent concentrations decreased to about 0.08 mg P/L in early August of 2012 from around 4.8 mg P/L at the beginning of July of 2012 after the bioreactor was constructed (Bell et al. 2015). Similarly, Fenton et al. (2016) reported higher dissolved reactive phosphorus concentrations from the effluent of a pilot-scale bioreactor compared to the DRP concentrations of the influent. The DRP concentrations of the effluent increased for roughly 3 months, but decreased by the end of the experiment (Fenton et al., 2016).

Choudhury et al. (2016) observed P losses for a biofilter composed of wood-chips and a 20 cm thick layer of sawdust in the middle of the filter. Dissimilar to the previous studies, the biofilter effluent was observed to have a mean SRP concentration of 1.9 mg L<sup>-1</sup>, which was not significantly different from the mean influent concentration of 1.5 mg L<sup>-1</sup> (Choudhury et al., 2016). Similarly, Zoski et al. (2013) reported removal efficiencies ranging only from 0% to about 10% for both TP and SRP by a bioreactor filled with wood-chips. Ranaivoson et al. (2012), on the other hand, observed bioreactors that were composed of wood-chips and reported a 79% average reduction of total phosphorus, 99% of which was soluble reactive phosphorus.

## 2.4 Phosphorus in Wetlands

Similar to bioreactors, the water levels in wetlands are variable, which helps create both an aerobic and anaerobic zone in the system (Reddy et al., 2005). Therefore, looking

at the phosphorus mechanics in a wetland can give some insight into how phosphorus could behave in a bioreactor based on the similarities between the two.

Phosphorus can move between the water column layers of a wetland through diffusion, but it is absorbed onto and released from soil minerals through precipitation and dissolution (Reddy et al., 2005). The retention and release of phosphorus depends on particular conditions including the C:P of the soil and solubility of phosphorus (Reddy et al., 2005, USEPA, 2008). Wetland soils with a high C:P would indicate that the soil doesn't have much P and so the soil would be able to absorb P more readily (USEPA, 2008). In contrast, soils with low C:P indicate that the soil has a large quantity of P and is more likely to release P.

Several factors influence the solubility of P in a wetland including pH, iron and aluminum oxides, calcium carbonate, clay content and redox potential (Eh) (Reddy et al., 2005). Inorganic P can be retained by iron and aluminum oxides along with calcium carbonate found in wetland soils, which reduces P solubility (Reddy et al., 1995). Higher pH soils typically contain calcium carbonate while lower pH soils typically contain iron and aluminum oxides (Reddy et al., 2005). Similar to the metal oxides in the soil, high clay content soils can absorb and retain P, decreasing P solubility (Reddy et al., 2005, USEPA, 2008). Soils in a wetland that contain large amounts of iron minerals that retain P are more stable under high Eh levels, while low Eh levels increase P solubility due to reduction (Reddy et al., 2005). Based on how P functions in a wetland system it could be possible that the solubility of P in a bioreactor could be determined using the same criteria.

## 2.5 Treatments in Bioreactors

Various treatments have been studied to reduce the amount of phosphorus in the effluent of a bioreactor. Alterations to the carbon source inside the bioreactor were looked at as one of the ways to reduce the loss of phosphorus in the effluent. Zoski et al. (2013) evaluated water treatment residual (WTR) as a phosphorus immobilizer in a bioreactor. WTR is a municipal by-product material that has gone through coagulation and flocculation, which leaves the residuals containing aluminum and iron oxides that can potentially immobilize P (Zoski et al., 2013). Zoski et al. (2013) observed three lab-scale bioreactors: one composed of just wood shavings, one where the first half of the bioreactor was made of WTR and the other half was made of wood shavings, and the final bioreactor was composed of a thoroughly mixed together combination of wood shavings and WTR. The two bioreactors that contained WTR were reported to remove more than 99% of TP and SRP from the effluent (Zoski et al., 2013).

Lassiter & Easton (2013) incorporated biochar into the bioreactor system with the wood-chip bed. Biochar is a type of organic carbon that comes from burning organic material and has the potential to adsorb phosphorus (Lassiter & Easton, 2013). The phosphorus concentration of the groundwater in Lassiter & Easton (2013) was on average 0.36 ppm, while the average phosphorus concentration of the biochar amended bioreactor effluent was 0.09 ppm. Results from this project showed that mixing biochar with the wood chips can potentially reduce SRP concentrations in the effluent by about 75% (Lassiter & Easton 2013). Similarly, Bock et al. (2015) observed the effects of biochar on the removal of nitrate and phosphorus in a wood-chip bioreactor using nine lab-scale



columns. Eight of the nine columns had biochar mixed in with the wood-chips and the ninth column was used as a control (Bock et al., 2015). Based on the experimental data, Bock et al. (2015) reported that the average effluent SRP concentration from the biochar amended columns was  $4.5 \text{ mg L}^{-1}$  lower than the effluent SRP concentration from the control column (61% SRP reduction).

Salo et al. (2015) observed the ability of steel by-products to adsorb phosphorus from a bioreactor effluent. An influent solution containing nitrate and phosphates was pumped through a vertical lab-scale wood-chip reactor and then through a lab-scale steel by-product reactor (Salo et al., 2015). The steel by-products were reported to reduce the phosphate concentration of the solution from  $0.45 \text{ mg P/L}$  to  $0 \text{ mg P/L}$  when the solution was pumped in at  $2.5 \text{ mL/min}$  (Salo et al., 2015). The phosphate concentration of the steel effluent was reported to be reduced to  $0 \text{ mg P/L}$  when under flow rates of  $5 \text{ mL/min}$  and  $10 \text{ mL/min}$  as well (Salo et al., 2015).

## 2.6 Bauxite Residue

Bauxite residue, commonly known as ‘red mud’, is a waste byproduct from aluminum oxide refining using the Bayer process. The Bayer process involves extracting aluminum oxide, commonly known as alumina, from bauxite ore. Bauxite ore is ground and then combined with sodium hydroxide (NaOH) under pressure and high temperatures to create a slurry (Xue et al., 2015). After the slurry goes through digestion, sodium aluminate is formed and then separated from the solids in the mixture (Xue et al., 2015).

The solids that are removed from the mixture are classified as bauxite residue. Bauxite residue contains silicates along with iron and aluminum oxides and is considered a waste product (Wang et al., 2010).

Various metal ions, such as iron and aluminum, may react with SRP and form insoluble compounds (Brady & Weil, 2010). Bauxite residue has been evaluated as a way to reduce the loss of phosphorus due to immobilization of SRP by the iron oxides present in it (Ward & Summers, 1993). In Australia substantial losses of phosphorus from fertilizers were found in the native sandy soils and to help remediate the phosphorus leaching, bauxite residue from Alcoa was neutralized with gypsum and incorporated into the soil, which resulted in a significant reduction in the amount of leached phosphorus (Ward & Summers, 1993). Wang et al. (2010) observed bauxite's ability to reduce the leaching of phosphorus from litter and manure. Two types of bauxite, red mud and brown mud, were each combined with poultry litter and cattle manure. Red mud is the actual waste by-product that comes directly from refineries while brown mud is the product of additional leaching and sintering of red mud (Wang et al., 2010). Brown mud was reported to reduce SRP by 40% in poultry litter and 70% in cattle manure while red mud reduced SRP by 27% in poultry litter and 55% in cattle manure (Wang et al., 2010). Though studies have been done on bauxite's ability to reduce the loss of phosphorus into water systems, research has yet to be done on the potential of bauxite residue to reduce the phosphorus in the effluent from bioreactors.

## 2.7 Summary

Phosphorus is an important nutrient for crop production. However, excess application of phosphorus can runoff and leach into water systems and overstimulate growth of aquatic plants and algae causing eutrophication. Conservation practices have been developed and studied to reduce the loss of phosphorus into the water systems. Though developed for reducing the loss of nitrate through tile drains, the potential for bioreactors to reduce phosphorus loss is uncertain. Engineering practices need to be developed to reduce the phosphorus losses for the conditions when a bioreactor enhances the phosphorus losses. Bauxite residue has been reported to immobilize phosphorus and reduce losses from soils and manure, but its effectiveness in reducing phosphorus losses from bioreactor effluent is not clear and should be evaluated.

## CHAPTER 3. METHODS

### 3.1 Anaerobic Water Columns

Three anaerobic water columns were constructed to monitor the change in nutrient concentrations caused by the wood-chips (Figure 3.1). The columns were constructed using 15.24 cm diameter PVC pipe cut to a length of 0.762 m, with a PVC sheet with a thickness of 1.27 cm adhered to the top and bottom of the PVC pipes using a waterproof silicone caulk. A small one-way air valve was purchased and installed in the top PVC sheet of the column to allow the gases in the column to be released without allowing the entry of air. Release of these gases prevented them from building up pressure and breaking the caulk seal on the columns. Two rubber stoppers were installed into each column for injecting a stock solution and extracting water samples from the columns. One rubber stopper was installed near the top end of the column just above the top of the wood-chips and used for refilling the column with a nitrate stock solution. The second rubber stopper was installed near the bottom of the column for extracting water samples. An oxidation-reduction potential (ORP) probe was installed just above the bottom stopper to ensure that the columns were remaining in an anaerobic state and to monitor the internal temperature of each column.

Each column was filled with 1.9 kg of air-dry wood-chips and 8 L of a 9.4 mg N/L nitrate stock solution made with deionized water. The wood-chips used in this experiment had been used in a previous month long run of this test. No phosphorus was added to the solution. Based on an analysis of the wood-chips that will be discussed in a later section of this chapter, the total mass of phosphorus that could be extracted from one column if the wood-chips were unused would be 475 mg P. This would give a maximum possible SRP concentration in the effluent of 59.375 mg P/L. The wood-chips used in this experiment were the same wood-chips used to construct the bioreactor at Throckmorton Purdue Agricultural Center in west central Indiana (Chichlowski, 2014). One of the major limitations for this experiment and all the following experiments with the wood-chips was that there was a very limited supply of wood-chips to use in these tests.

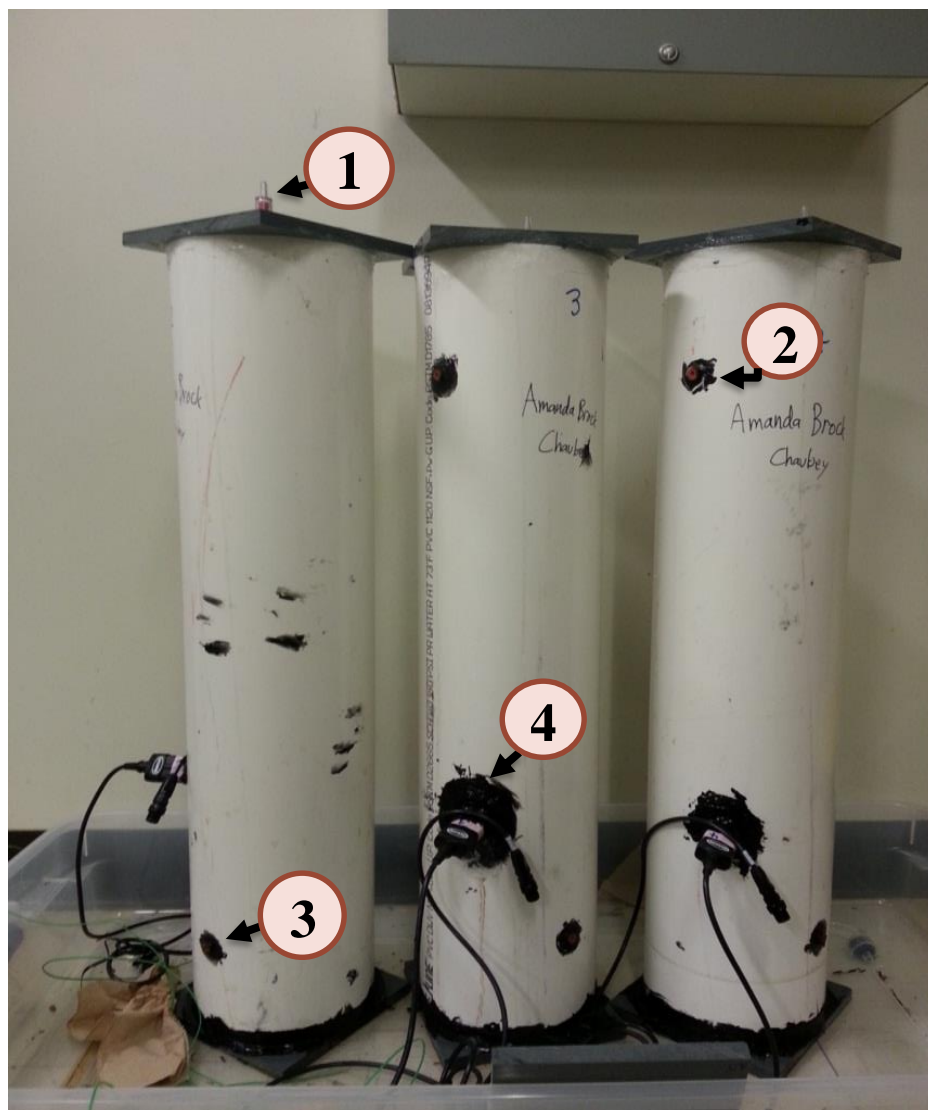


Figure 3.1: Three anaerobic water columns each with: one-way air valves (1), a rubber stopper for refilling (2), a rubber stopper for taking samples (3) and ORP probes (4). The contents within are wood chips and a nitrate solution.

Sampling began roughly 12 hours after the nitrate solution was added and the tops of the columns were sealed. Water samples of 50 mL were taken twice a day for 55 days and stored in 50 mL brown bottles in a freezer until they could be analyzed. After every

sampling, 50 mL of the nitrate stock solution was injected back into the columns so that the water volume remained constant throughout the experiment. The temperature and ORP level was recorded every time that a sample was taken. Samples were vacuum filtered using a twelve port filtration manifold and 0.7  $\mu\text{m}$  glass microfiber filter paper.

### 3.2 Aerobic Degradation

To better understand the impact of wood-chips on the release of phosphorus from the columns, a separate test under aerobic conditions was performed after the column test was finished. The scale of the experiment was reduced compared to the original column test. From each of the original water columns a set of three jar replicates was constructed giving a total of nine jars (Table 3.1). The replicates were constructed using wood-chips from their corresponding water column. Each replicate was filled with 40 grams of wood-chips (Figure 3.2). A 300 mL volume of the same 9.4 mg N/L nitrate solution used for the water columns was also added to each replicate. The jars were then placed on an orbital shaker table that continuously swirled the water in the jars at 180 rpm to keep them aerobic by enabling air diffusion into the overlying water column. Before each sampling the jars were taken off the shaker table and vigorously shaken by hand.

Table 3.1: Setup of the replicate sets for each anaerobic water column.

Water Column 1	Water Column 2	Water Column 3
Set 1	Set 2	Set 3
Replicate 1	Replicate 1	Replicate 1
Replicate 2	Replicate 2	Replicate 2
Replicate 3	Replicate 3	Replicate 3



Figure 3.2: Nine jars, three replicates for each column, filled with wood-chips and a nitrate solution. They are placed on a rotational shaker table.

The main experiment was run for two weeks. During a prototype run of this experiment, SRP concentrations were found to have stopped increasing after five days. Based on the results from the prototype experiment, no tops were placed on the jars for



the first five days to avoid causing anaerobic conditions to develop. After five days, to prevent subsequent evaporation, lids were placed on top of the jars to reduce evaporation losses. During the experiment, DO concentration measurement in the water was not possible due to the jars shaking vigorously thereby making it impossible to set an oxygen probe in place for the measurement.

A validation test for DO concentration was performed after the experiment was completed. A jar was filled with 40 g of wood-chips and 300 mL of DI water. The jar was swirled at 180 rpm on an orbital shaker table for 48 hours. After 48 hours the jar was removed from the table and the DO concentration was immediately measured using an oxygen probe and a table-top meter. The DO concentration of the water was also measured while the jar was being hand stirred at a less vigorous pace. The DO concentration of the jar immediately after being removed from the shaker table and while being hand stirred was 3.81 mg/L and 6.41 mg/L respectively. The DO measurements from both readings were above 1 mg/L, indicating that the jar was aerobic (Dinicola, 2006).

Samples were vacuum filtered using a filtering flask, a crucible, a filter tube, and glass microfiber filter paper (Figure 3.3). For the first two days a 20 mL sample was taken twice a day and only once per day after that. Similar to the column test, the water that was taken out was replaced with the stock nitrate solution to keep the water volume constant. Samples were put into 50 mL brown bottles and taken back to the laboratory for analysis. The water samples taken from the jars were filtered using a 1.5  $\mu\text{m}$  filter and then placed in a freezer until they were ready to be analyzed.

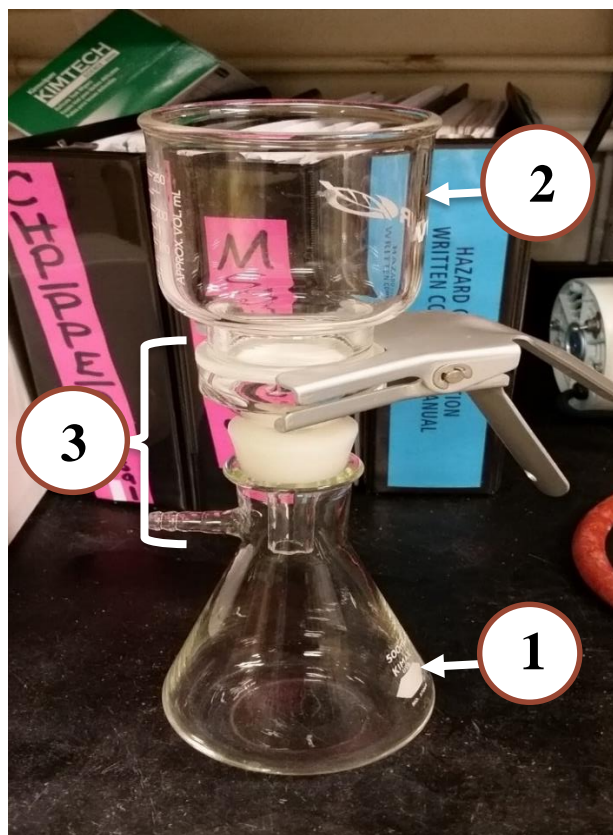


Figure 3.3: Filtration system consisting of a filtering flask (1), crucible (2), and filtering tube with fritted disk (3).

### 3.3 Sterilized Wood-chip Anaerobic Jars

The anaerobic water columns mention previously had three replicates. However, different SRP concentrations were observed for each column. During the disassembly of the anaerobic water columns, fungi were found growing on the wood-chips of two of the three columns. To determine if fungus could be affecting the release of phosphorus from the wood-chips, a comparison was done between non-sterilized wood-chips and sterilized wood-chips. The wood-chips used in this experiment were from the same source as the

wood-chips used for the anaerobic water columns. After being wetted, 120 g of wood-chips were placed in a Heidolph Tuttner 2540 manual autoclave for 30 minutes at a temperature of 121 °C and a pressure of 1.2 bar. After the sterilization, the wood-chips were exposed to ambient air on a table for about 24 hours before being placed in the autoclave again. This process was repeated 4-5 times to make sure that all fungi in the wood-chips were killed. Once sterilization was complete, 40 g of sterilized wood-chips were placed in two mason jars and a beaker with similar diameter to the jars. Two additional jars and a beaker were then filled with 40 g of wood-chips that had not been sterilized giving three replicates of non-sterilized wood-chips and three replicates of sterilized wood-chips. Two of the non-sterilized jars had an ORP probe placed in them to monitor anaerobic conditions. Each jar was then filled with 250 mL of a 9.4 mg N/L nitrate solution, had Parafilm placed over the tops and were then wrapped in aluminum foil to keep out light. A hole was cut out of the Parafilm of each jar to facilitate water sampling with a pipette. These holes were covered again with a small piece of Parafilm during incubation periods.



Figure 3.4: Sterilized wood-chip test with jars wrapped in aluminum foil and two jars having ORP probes placed in them.



Figure 3.5: Hole in the Parafilm for pipette sampling.

The experiment was conducted over the course of five days. On the first day only one sample was taken. During the next three days, samples were taken five times a day. On the last day, four samples were taken. During each sampling a 20 mL water sample was collected. The first sample was taken two hours after the experiment began. For the remaining four days the daily sampling period started around 8 AM and each subsequent sample was taken at two hour intervals. After a sample was taken, the jar was refilled with the 9.4 mg N/L nitrate solution to bring the solution back to the initial volume. Values of ORP and temperature were recorded before each sampling. No phosphorus was added to the stock solution.

### 3.4 Bauxite Residue Transformation

Red mud bauxite residue was studied as a possible remediation for phosphorus observed in a bioreactor's effluent. An attractive property of bauxite residue, as previously described in Chapter 2, is its capacity to retain phosphorus. However, bauxite residue has negative properties as well. 80-90% of bauxite residue occurs as red mud (Xue et al., 2016), which looks and feels like slightly wet soil. The particles in the red mud range in size from 2 to 20  $\mu\text{m}$  (Xue et al., 2016). Also, Kolencsik-Toth et al. (2014) has reported that red mud can have a hydraulic conductivity ranging from  $1 \times 10^{-9}$  to  $2 \times 10^{-8} \text{ m s}^{-1}$ . The hydraulic conductivity and particle size of red mud suggest that bauxite residue cannot be put directly in the tile drainage pipe for risk of causing a blockage in the pipes.

To decrease the risk of causing a blockage, the loose bauxite residue was compacted and sintered into a solid disk form with a diameter of about 3.81 cm and a thickness of 0.953 cm (Figure 3.6). All the bauxite disks used in this study were made by a PhD student in the Material Science Engineering Department at Purdue University. Different increments and types of materials were added to the bauxite residue before compression. These added materials included Parrafin wax, solid salt and aqueous salt. After the bauxite mixture was made into disks either the heat from the sintering process would melt the added material or the added material would dissolve in water once the disk was saturated. The removal of the additive leaves pores in the disks that increase the surface area of the disk and better allow water to flow through the disk. For the following experiments with the bauxite disks there were two major limitations. There was a limited number of bauxite disks to run tests on as the disks were being made by hand by a student. The other limitation was that once a disk was used for absorbing phosphorus it couldn't be used again as it would not be possible to efficiently remove the phosphorus from the disks.



Figure 3.6: Solidified bauxite disk against a tape measure to show the diameter and size of the bauxite samples.

### 3.5 Bauxite Disk Flow Tests

A test was performed to determine how efficiently water could flow through the bauxite disks. This test was done to determine viable methods for implementing the bauxite disks into the field bioreactor. The same filtration system used in the aerobic degradation test was used for this test (Figure 3.3). The bauxite disk was placed inside the crucible and onto the filter tube. 200 mL of DI water was then poured into the crucible and left to drain. It was assumed that the water would move through the bauxite disk and into the filtering flask. This assumption was made due to the bauxite having an almost equivalent diameter as the crucible mouth. However, some of the water could bypass the bauxite disk by flowing around the sides of the disk. In an attempt to keep water from

bypassing the bauxite disk, a rubber glove was tightly wrapped around the disk with a rubber band while 100 mL of DI water was poured in through a hole created at the top of the glove. This method kept water from bypassing the disk. From this test it was observed that the bauxite disks held the water after becoming saturated and only allowed the water to pass through at a slow drip. During one run of this test only 2-3 drops of water came out of the bauxite disk over the course of a 15-minute period. However, this did not affect the possibility of use in a bioreactor.

### 3.6 Phosphorus Absorption by Bauxite Disks

Three different types of bauxite disks were tested for phosphorus absorption. The types of bauxite used were: plain bauxite disks, bauxite disks with altered pH and bauxite disks with salt (NaCl) added. Three bauxite disks with varying pH levels were selected for testing the effect of bauxite pH on phosphorus absorption. Additionally, three bauxite disks with varying NaCl concentrations were selected to test the effect that salt has on the phosphorus absorption of the bauxite. The first attempted method to look at the ability of the bauxite to absorb phosphorus was through the use of the same filtration system mentioned in previous sections (Figure 3.3). A plain bauxite disk was placed in the crucible on the 1.5-micron filter paper. A 1 mg P/L phosphate solution of volume 200 mL was made using DI water. The phosphate solution was poured into the crucible and onto the bauxite disk. The solution flowed through and around the bauxite and then through the filter tube into the filtering flask. A 10 mL sample was taken from the solution in the flask and then the solution was run through the bauxite and filtering system again. This



process was repeated seven times. This method was used assuming that the phosphate solution flowing through the filtration system would be similar to a possible field setup. However, the results from this method of testing were not reliable, so a different method was attempted.

The second method applied for testing phosphorus absorption by the bauxite disks was to leave the bauxite sitting in a beaker filled with a phosphorus solution. This method was used to test bauxite disks with altered pH levels and bauxite disks with salt mixed in. Three bauxite disks with pH levels of 5, 7 and 9 were tested over a two-week period. Each disk was placed in a separate 500 mL beaker. A 2 mg P/L phosphate solution at a volume of 250 mL was made for each beaker. An initial sample of 25 mL was taken from each solution before it was introduced to the bauxite disks. After the phosphate solution was added to the beakers, Parafilm was placed over the tops of each beaker so as to prevent evaporation of the solution. Aerobic conditions were most likely prevalent through this test, but it is uncertain if the condition of the beakers truly was aerobic since neither the ORP or DO levels were measured. Sampling began one week after the solution was added to the beakers. Four 20 mL samples were taken at random points during the second week. No SRP solution was added back into the beakers to replace what had been taken. A summary of the experimental setup is provided in Table 3.2.

Three bauxite disks with varying amounts of NaCl mixed in were tested next. The actual percent of NaCl mixed in the bauxite disks used for this experiment is unknown. These bauxite disks each had a number written on them (1, 3 and 5) by the PhD student in the Material Science Engineering Department who made the bauxite disks, so it was

assumed that the disks contained 1%, 3% and 5% NaCl. These NaCl disks will be referred to by their marked numbers throughout this document. As previously mentioned, salt was added to the bauxite residue to increase porosity in the bauxite disk once the salt dissolved out of the disk. It was hypothesized that the greater the amount of salt in the disk the greater amount of pore space and thus more surface area available for phosphorus sorption.

Based on results from the altered pH bauxite test, the running time for this test was shortened to a 24-hour test. Similar to the test with the differing pH bauxite, each salt bauxite disk was placed into an individual container and a 2 mg P/L solution at a volume of 250 mL was made for each container. To better keep the solution mixed, these samples were placed on an orbital shaker table. Mason jars were used as the containers instead of beakers because the beakers could not fit into the slots on the table. An initial sample of 20 mL was taken from each solution before they were poured into the jars. Six subsequent samples of 20 mL were taken at random points of time during the 28-hour period. No SRP solution was added back into the jars to replace what had been taken. All samples were filtered before being analyzed using a 1.5  $\mu\text{m}$  filter. A summary of the experimental setup is provided in Table 3.2.

Table 3.2: Experimental parameters for phosphorus absorption tests of bauxite

Bauxite Type	Number of Disks	Solution Conc. (mg P/L)	Initial Sample Volume (mL)	Sample Volume (mL)	Time of First Sampling	Length of Experiment
pH (5, 7 & 9)	3	2	25	20	1 week	2 weeks
NaCl (1, 3 & 5)	3	2	20	20	1 hour	28 hours

Preliminary results from the phosphorus absorption test with the salt mixed bauxite disks seemed to indicate that absorption began to occur quickly. To better understand the phosphorus absorbing ability of the bauxite, a one-hour phosphorus absorption test was performed. A bauxite sample with 3% NaCl added to the mix was used for this experiment. A 2 mg P/L solution at a volume of 500 mL was made and an initial sample of 15 mL was taken. The remainder of the solution was poured into a jar and placed onto a shaker table. Once the bauxite was added to the jar the table was turned on. A sample was taken every two minutes with a total of 31 samples collected during the experiment. Initially, the samples taken were 15 mL, but this volume was reduced to 12 mL at 42 minutes into the test to prevent the volume of solution from getting too low. The samples from this experiment were filtered using nylon 0.45  $\mu\text{m}$  syringe filters before analysis to remove any free floating bauxite.

### 3.7 Lab-scale Outflow Box with Bauxite

To understand how the bauxite would perform once applied to the bioreactor, a lab-scale version of the bioreactor's outflow box was created. When scaling down the dimensions of the outflow box the hydraulic residence time (HRT) of the lab-scale box needed to be the same as the average HRT of the field scale outflow box at TPAC. Using flow data from the field bioreactor at TPAC (Chichlowski, 2014), an average flow rate of  $0.016 \text{ m}^3/\text{min}$  was determined for the outflow box. The volume of the water filled side of the field outflow box was measured with the height of the box going to the bottom of the V-notch. The average HRT of the field bioreactor was calculated by dividing the volume of the water filled side of the outflow box ( $V$ ) by the average effluent flow rate ( $q$ ) (Equation 3.1). The average HRT of the field outflow box was determined to be 1.32 minutes. An aquarium pump with a flow rate of 3.5 gph or  $2.21 \times 10^{-4} \text{ m}^3/\text{min}$  ( $q_p$ ) was acquired and the required volume of the box was determined by multiplying the pump's output flow rate by the average HRT of the field outflow box (Equation 3.2). By setting the length ( $l$ ) and width ( $w$ ) of the box to 0.0508 m the height of the box ( $h$ ) was determined to be 0.113 m.

$$HRT = \frac{V}{q} \quad \text{Equation (3.1)}$$

$HRT$  = hydraulic residence time (min)

$V$  = Outflow box volume to bottom of V-notch ( $0.0211 \text{ m}^3$ )

$q$  = average effluent flow rate ( $0.016 \text{ m}^3/\text{min}$ )

$$h = \frac{q_p * t}{l * w} \quad \text{Equation (3.2)}$$

$h$  = height of lab-scale box (m)

$q_p$  = flow rate of pump ( $2.21 * 10^{-4} \text{ m}^3/\text{min}$ )

$HRT$  = hydraulic residence time (min)

$l$  = length (this was set to be 0.0508 m)

$w$  = width (this was set to be 0.0508 m)

The box was constructed from an acrylic sheet cut into pieces and then sealed together with clear silicone caulk. A hole was drilled into one of the sides at the bottom of the box for a 0.188 cm diameter tube to fit into. The tube connects the water pump to the system. On the opposite side of the box a V-notch was cut at the top for water to flow through and out of the box. In this way, water would flow through the box with a similar flow path to the field bioreactor (Figure 3.7).

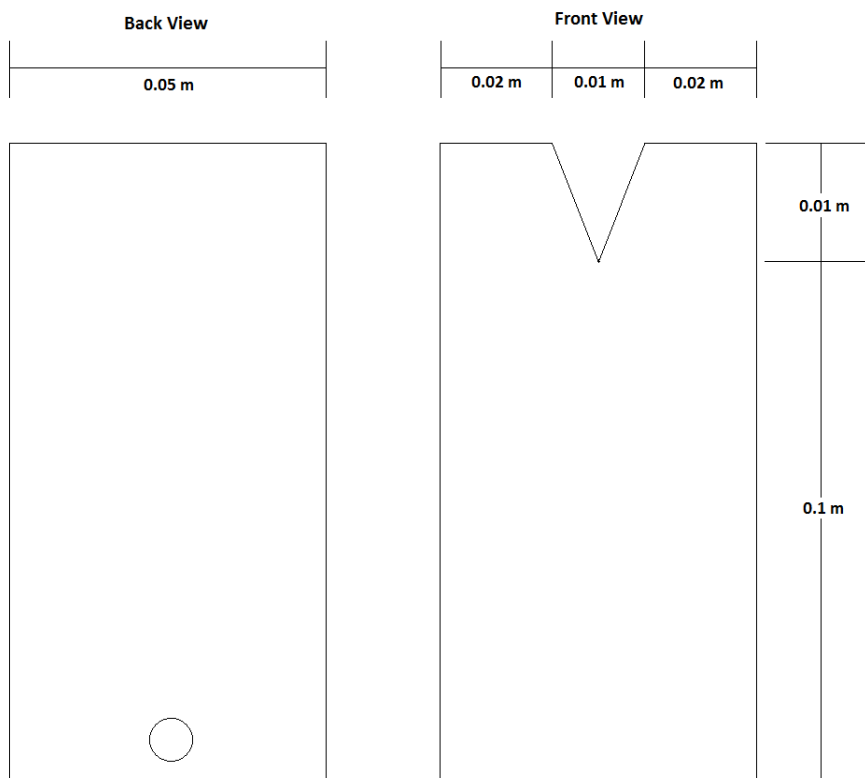


Figure 3.7: Diagram showing the back (left) and front (right) of the lab-scale outflow box. The two sides of the box have the same dimensions as the back view.

Bauxite disks made with 1% and 5% NaCl were used in this test to determine how well phosphorus could be absorbed from the flowing water. These disks were each initially placed in DI water for 24 hours to allow for the salt in them to dissolve, allowing for more pore space and surface area for the phosphorus to bind to. They were then oven dried, weighed for their mass and prepared for the experiment. A fishing line was tied two ways around the bauxite so as to securely hold it without allowing it to slip out. The ends of the lines were then tied around the middle of a tongue depressor leaving a length

that would allow the bauxite to be suspended in the water about half way down the length of the box (Figure 3.8). To prevent putting stress on the box, two jars were placed on pieces of PVC sheet on either side of the box and the ends of the depressor were placed on the jars (Figure 3.9). Suspending the bauxite by using the depressor allowed for the bauxite to be easily removed from the box.

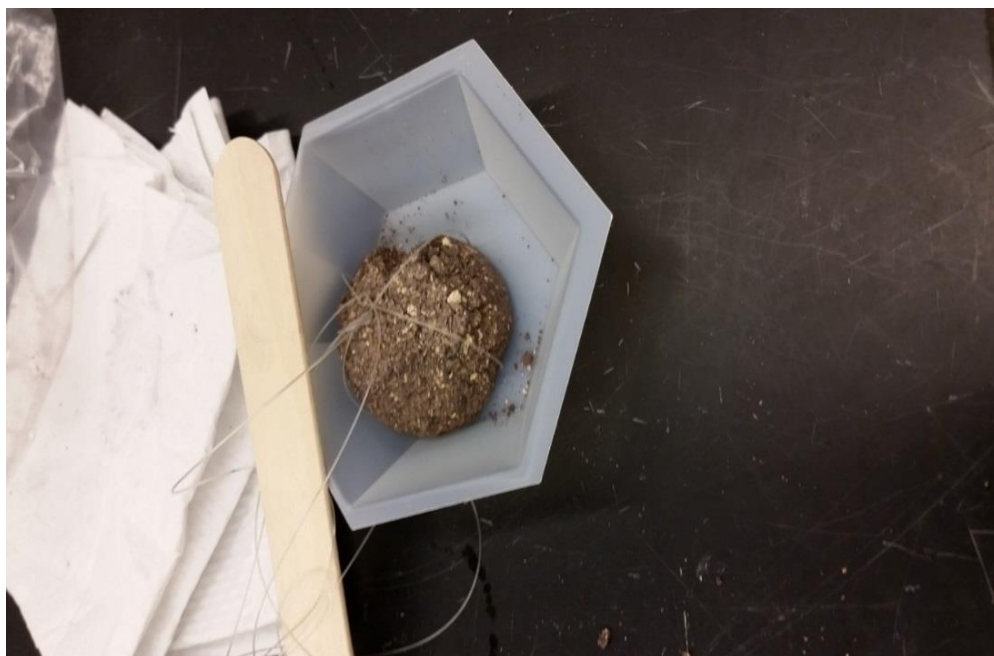


Figure 3.8: Fishing line is tied around a bauxite disk and then tied around a tongue depressor.



Figure 3.9: Two pieces of PVC sheet are placed next to the lab-scale outflow box and two jars are placed on the sheets to allow the bauxite to be suspended in the box.



Figure 3.10: Complete experiment setup. A large container holds the input phosphorus solution and a tube connecting to the pump is placed inside. Another tube goes into the clear box where the solution is continually pumped.



Samples were taken from the water flowing through the V-notch weir. At first the samples were taken every 1-3 minutes to ensure that any immediate reactions that occurred were captured once the bauxite was placed in the box. The sampling was repeated every 15 minutes after the fifteen-minute mark was reached in the experiment for both bauxite disks. The samples were analyzed for SRP immediately after sampling. This experiment was run until the observed SRP concentrations of the effluent returned to the initial concentration.

### 3.8 Sample Analysis

Water column samples and most bauxite water samples were analyzed for Nitrate-N ( $\text{NO}_3\text{-N}$ ) and soluble reactive phosphorus (SRP) using a colorimetric test that was performed by a Seal AQ2 Auto Analyzer. The method used to test for  $\text{NO}_3\text{-N}$  ( $\text{NO}_x$ ) was EPA-114-A Rev. 9, which is equivalent to USEPA Method 353.2 and has a minimum detection limit of 0.03 mg N/L. In this method, nitrate was reduced to nitrite through the use of a cadmium coil and then detected by using a sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride reagent. The analysis for SRP ( $\text{o-PO}_4$ ) was done using the AQ2 method EPA-118-A Rev. 5, which is equivalent to USEPA Method 365.1 and Standard Method for Examination of Water No. 4500-P E and has a minimum detection limit of 0.003 mg P/L. To detect SRP in this method, ammonium molybdate and antimony potassium tartrate reagents are combined with ascorbic acid in a sample. This combination results in a blue color that can be measured for absorbance.

Samples taken for the lab-scale outflow box test were analyzed for SRP using the Standard Method for Examination of Water No. 4500-P E. Standards were made and the absorbance of each standard was recorded and plotted against the known concentration. Adding a linear trend line to this plot gave the equation to obtain the SRP concentrations of the samples taken based off of the absorbance.

## CHAPTER 4. RESULTS AND DISCUSSION

### 4.1 Anaerobic Water Column Test

All three anaerobic water columns exhibited an increase in soluble reactive phosphorus (SRP) (Figure 4.1). However, the SRP concentrations varied greatly among the columns. The increase in SRP concentration over time was the least for Water Column 1. In contrast, Water Column 2 reached a maximum SRP concentration of 4.5 mg P/L over the course of thirty-four days (Figure 4.1). Change in SRP concentration was intermediate for Water Column 3 with a maximum concentration of 0.6 mg P/L observed during the experiment. The nitrate concentrations for all three columns reduced to ~0.01 mg N / L within three days after the initiation of the experiment and stayed at this concentration for the remainder of the experiment (Figure 4.2).

During the course of this experiment, leaks were discovered in Water Column 1 and Water Column 3. To fix the leaks, the columns were opened and the contents were removed. The water was separated from the wood-chips and stored in a sealed container until the leak was repaired. Repair time ranged from 3-9 days. An assumption was made that separating the water from the wood-chips stopped the reaction that caused the release of phosphorus from the wood-chips to the overlying water column. The days that the

experiment was stopped to repair the leaks where not counted, which is why each water column runs for a different number of days in Figure 4.1.

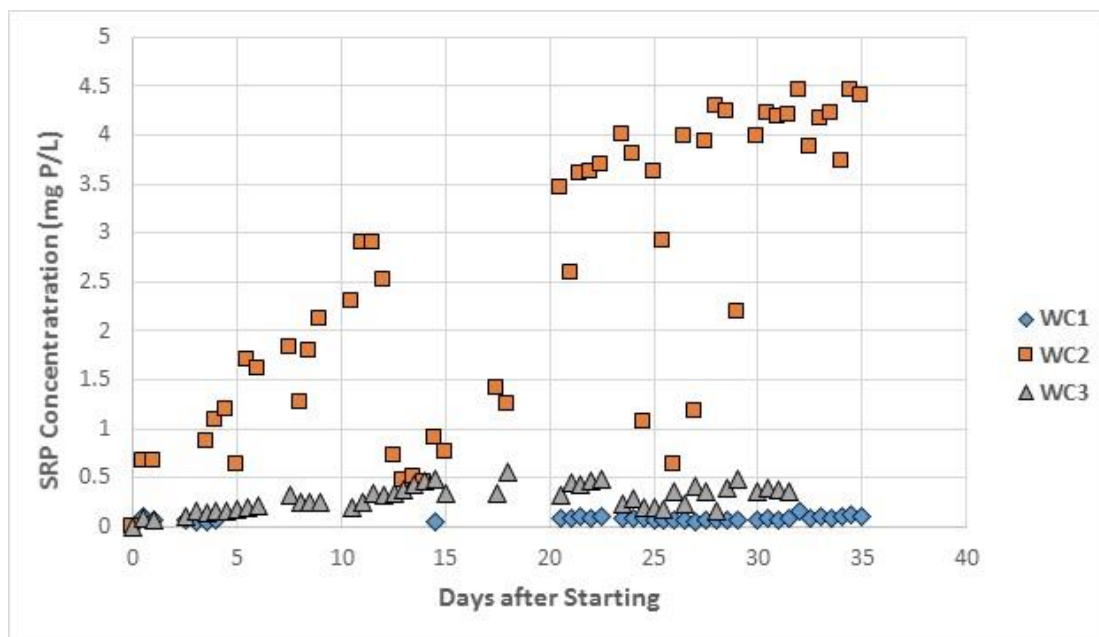


Figure 4.1: The SRP concentration of samples taken from the three anaerobic water columns over time. Water Column 1 (WC1), Water Column 2 (WC2) and Water Column 3 (WC3).

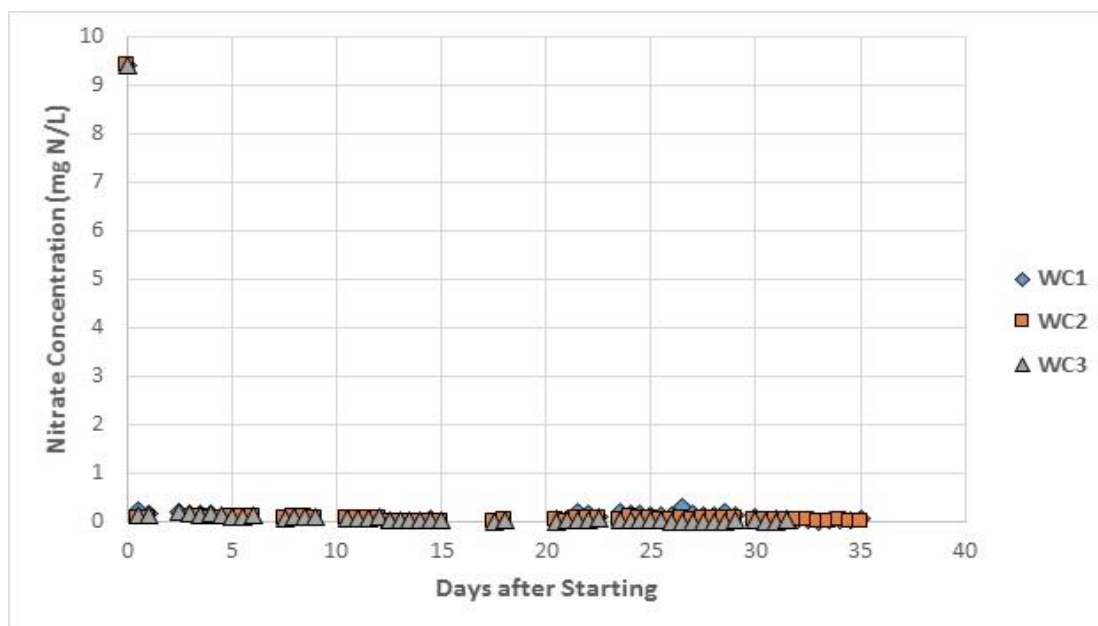


Figure 4.2: Nitrate concentration of the anaerobic water columns over time.

The water columns were considered anaerobic for negative ORP levels and aerobic for positive ORP levels. The ORP levels for all three columns remained below 0 mV throughout the duration of the experiment (Appendix A: Figure A.1 or Table A.4). The negative ORP levels indicate that the water columns remained anaerobic throughout the experiment. When newly repaired, the columns exhibited negative ORP levels close to 0 mV due to the water being exposed to the air. However, within 12 hours the ORP levels decreased to around -300 mV. The internal temperature of the columns remained around 20 °C, ranging from 19 °C to 22 °C. The ORP and temperature trends during the experiment are provided in Appendix A.

After the experiment was completed the water columns were disassembled. During disassembly a fungal growth was discovered in two of the three columns. Water Column 2 had a large amount of fungus netting throughout the wood-chips. In contrast, Water Column 3 had small specks of yellow fungus on some of the wood-chips. Water Column 1 had no observable fungal growth. It is likely that Water Column 1 did not develop fungal growth due to the column being under repair twice for leaks during the experiment. The first leak occurred 4 days after the experiment was started and took 9 days to repair before the column could be restarted. The second leak occurred 15 days after the experiment was started. Repairs for the second leak took 3 days. On a visual inspection, Water Column 2 had the largest visible amount of fungus and had the highest observed concentrations of SRP. Similarly, Water Column 1 had no visible fungus and showed the lowest observed increase in SRP concentration.

#### 4.2 Aerobic Water Column Test

The average SRP concentrations for each column initially increased under aerobic conditions (Figure 4.3). The peak concentrations were reached within 1 to 6 days after the initiation of the experiments and then reduced during the subsequent sampling events. The replicates for Water Column 1 reached an average peak of 0.2 mg P / L after three days and leveled off to an average concentration of 0.03 mg P / L (Table 4.1). It should be noted that after each sampling the jars were refilled with a nitrate stock solution. Figure 4.3 shows that for Water Column 1, SRP concentration was increasing for the first six days of the experiment. Interestingly, nitrate concentrations in all the Water Column 1

replicates decreased to 0.1 mg N / L within a day and stayed at this concentration for the remainder of the experiment (Figure 4.4).

The Water Column 2 replicates reached a maximum average SRP concentration of 1.2 mg P/L within the first five hours of the experiment, but then decreased to ~0.1 mg P / L in 24 hours. The average SRP concentration then began increasing again until it reached a second peak of 0.5 mg P / L five days into the experiment. After five days the average SRP of the Water Column 2 replicates began decreasing and leveled off to 0.1 mg P / L (Table 4.1). These SRP concentrations were much lower than the SRP concentrations seen for Water Column 2 in the anaerobic test. The initial spike was the very first sample taken from these replicates.

Prior to being used for the aerobic test, the wood-chips had been used in the anaerobic water columns test and underwent some degradation. After the water column test was completed the wood-chips were left to air-dry for 3 months. When collected for use in the aerobic degradation test, the wood-chips from Water Column 2 felt brittle. The initial wetting of the wood-chips and movement of the water due to the shaker table could have caused the brittle wood-chips to break apart. The breaking of the wood-chips could possibly release some phosphorus, which could explain the observed concentration spike. As with the Water Column 1 replicates, the nitrate concentrations of the Water Column 2 replicates decreased to 0.1 mg N / L and remained at this concentration. The nitrate decrease occurred at two days into the experiment.

The average SRP concentration of the Water Column 3 replicates reached a peak of 0.1 mg P / L after two days and leveled off at 0.02 mg P / L (Table 4.1). After 24 hours

the average nitrate concentration of the Water Column 3 replicates decreased to 0.1 mg N / L and remained relatively constant for the remainder of the experiment (Figure 4.4).

Similar to Water Column 2, the SRP concentrations of Water Column 3 were lower than the SRP concentrations seen for Water Column 3 in the anaerobic test.

The decrease in nitrate concentration observed in the aerobic test was not expected since denitrification is typically an anaerobic process. An analysis of the wood-chips revealed that they contain 483.4 mg C/gr dry wt., 0.25 mg P/gr dry wt. and 4.7 mg N/gr dry wt. giving it a C:N of 103:1. This ratio indicates that the wood-chips are lacking in nitrogen and the microorganisms in the system require nitrogen to function. Since the microorganisms cannot get nitrogen from the wood they may be using the nitrogen in the overlying water column solution. This would cause the nitrate concentration of the water to drop even under aerobic conditions.

When comparing the averages for all three replicate sets in Figure 4.3, it can be seen that the Water Column 2 replicates had the highest concentrations of SRP, similar to the results from the anaerobic column tests. The aerobic maximum average SRP concentration of Water Column 2 was 1.2 mg P/L (Table 4.1). The Water Column 3 replicates, however, had the lowest concentrations in the aerobic test while Water Column 3 actually had the second highest concentrations in the anaerobic column test. The aerobic maximum average SRP concentration for Water Column 3 was 0.1 mg P/L while the maximum average SRP concentration for Water Column 1 was 0.2 mg P/L (Table 4.1).



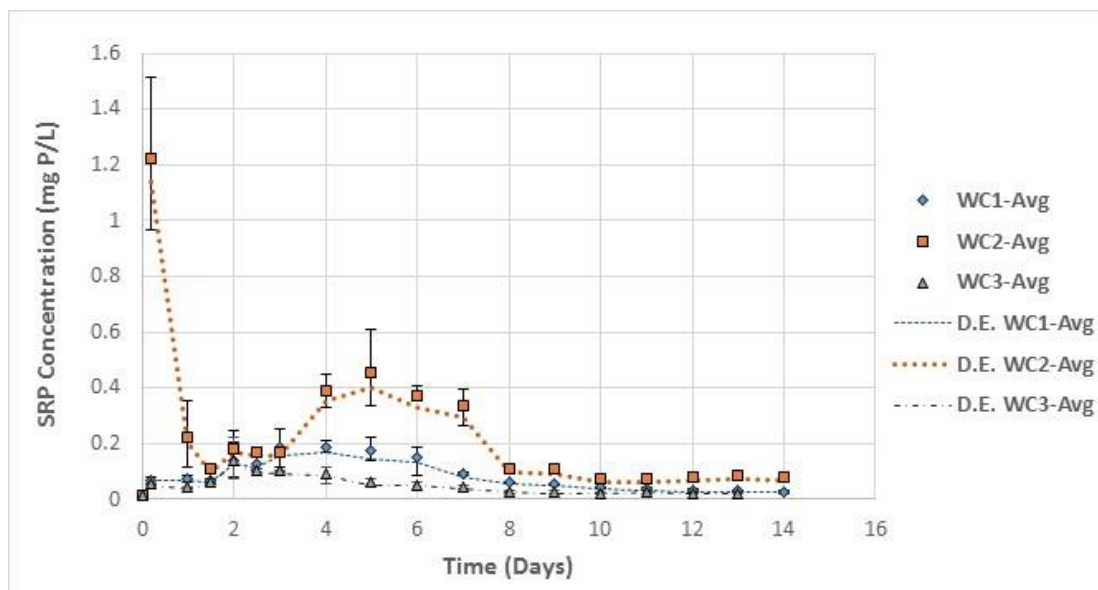


Figure 4.3: The average SRP concentration of each replicate set over the course of the experiment with error bars. The error bars represent the range of the SRP concentration from the three replicates. The dashed lines are the SRP concentration of the solution after accounting for the dilution effect (D.E.) of refilling.

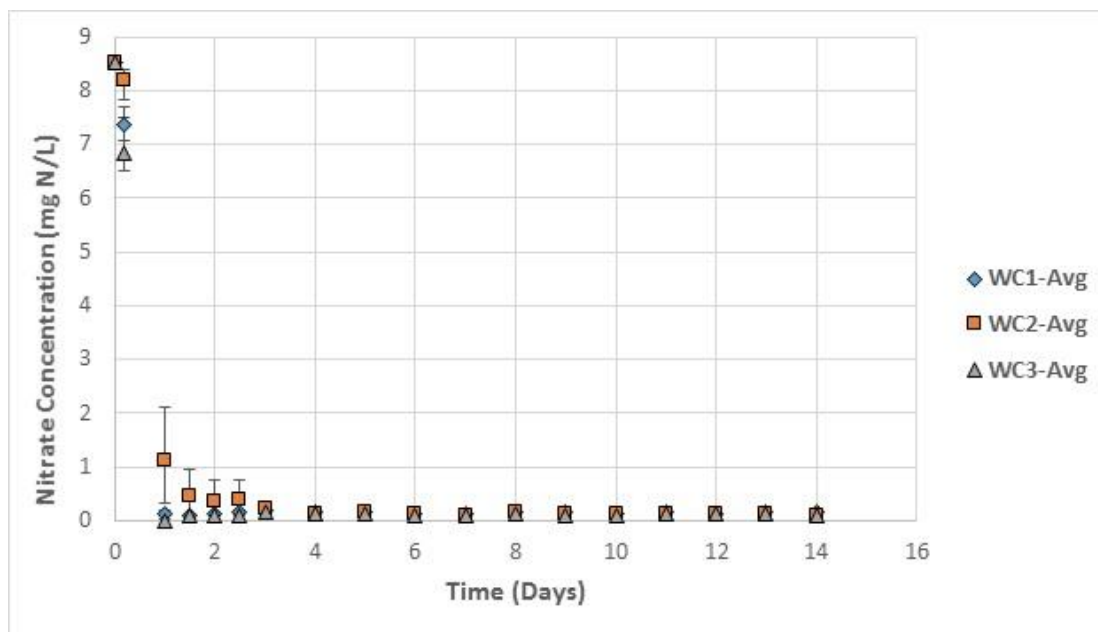


Figure 4.4: The average Nitrate concentration of each replicate set over the course of the experiment with error bars. The error bars represent the range of the nitrate concentration from the three replicates.

Table 4.1: The average maximum and final SRP concentrations for each set of water column replicates.

	Average Maximum SRP Conc. (mg P/L)	Average Final SRP Conc. (mg P/L)	Average Time to Peak (days)
<b>Water Column 1 Replicates</b>	0.2	0.03	3
<b>Water Column 2 Replicates</b>	1.2	0.1	0.2
<b>Water Column 3 Replicates</b>	0.1	0.02	2

Overall, the average maximum SRP concentrations under aerobic conditions were substantially lower than the maximum SRP concentrations under anaerobic conditions

with the exception of Water Column 1 (0.2, 4.5, 0.6). This difference could be partially attributed to a difference in the wood-chips. The wood-chips in the anaerobic test were previously used in an early run of the test. The wood-chips used in the aerobic test were from the second run of the anaerobic test and had gone through over 2 months of degradation.

### 4.3 Sterilized Woodchips Test

To determine if fungal growth affected the release of phosphorus from the wood-chips, a comparison was done between sterilized wood-chips and non-sterilized wood-chips. Three replicates were made for the sterilized wood-chips and three replicates were made for the non-sterilized wood-chips. All six jars started with the same nitrate solution with a concentration of 9.6 mg N/L and no added phosphorus. The SRP results for both sets of jars were very similar with the exception of the maximum (Figure 4.5). The average SRP concentration of the sterilized wood-chips reached a maximum concentration of 21.8 mg P/L after 19 hours into the experiment. The average SRP concentration of the non-sterilized wood-chips reached a maximum of 18.9 mg P/L at the same time. After 19 hours into the experiment, the average SRP concentration for both sets of wood-chips steadily decreased to a final concentration of ~5 mg P/L (Table 4.2). It should be noted that the final SRP concentrations were still much higher than the initial concentration of 0 mg P/L. The sharp decreases observed during the day and almost constant SRP concentration over-night are likely due to day time sampling removing more phosphorus from the solution than is being added into the solution from the wood-

chips (Figure 4.5). These results seem to indicate that the fungus does not affect the amount of phosphorus released from the wood-chips, which is not what was hypothesized based on the anaerobic water column results.

A possible explanation for why it appeared that the amount of fungus in the columns was correlated with the SRP concentrations is the repairs of the columns that occurred in the anaerobic column test. As previously mentioned, when a leak occurred the column had to be emptied and repaired. The water was separated from the wood-chips during repairs so that any reactions that were occurring in the column were halted. The remaining columns, however, were not stopped when one column was being repaired meaning that decomposition was still occurring with the wood-chips in the functioning columns. By the time the broken column was fixed the wood-chips of the other columns had lost more phosphorus than the wood-chips of the newly repaired column.

Also, as previously mentioned, the wood-chips had been used in a previous run of the column test. During this previous run Water Column 2 only ran for roughly 2 days and then was taken apart for repairs for the remainder of the run. Water Column 1 and Water Column 3, however, continued to run for a month. The wood-chips in the two running columns would have lost phosphorus and the wood-chips in the non-running column would have retained most of their phosphorus by the time they were used in the second run of column test. The combination of the wood-chips being used in a previous run and the different amounts of time that each column was running during the second run of the test could explain the large difference seen in the SRP concentrations of the water column effluents.

The previous use of the wood-chips can also explain why the SRP concentrations fluctuate between the three experiments with the wood-chips. Wood-chips in the anaerobic water column test had been previously used in a month long run of the column test before being used in the second run of the column test. The wood-chips used in the aerobic test were from the second run of the column test after the two-month long test was finished. For the sterilized test the wood-chips used were previously unused. Each set of wood-chips having a different amount of previous use before the experiments would indicate that the wood-chips contain different amounts of phosphorus, which would affect the SRP concentrations of the solutions.

The nitrate concentrations differed between the sterilized and non-sterilized wood-chips. The average nitrate concentration of the sterilized wood-chips decreased to ~6 mg N/L within two hours of the experiment starting (Figure 4.6). This 6 mg N/L concentration was maintained until two days after the experiment was started. At the end of the experiment, the average nitrate concentration of the sterilized wood-chips was 0.7 mg N/L (Table 4.2). The average nitrate concentration of the non-sterilized wood-chips decreased to ~0 mg N/L twenty-four hours into the experiment (Table 4.2). For the remainder of the experiment the average nitrate concentration remained around 0 mg N/L.

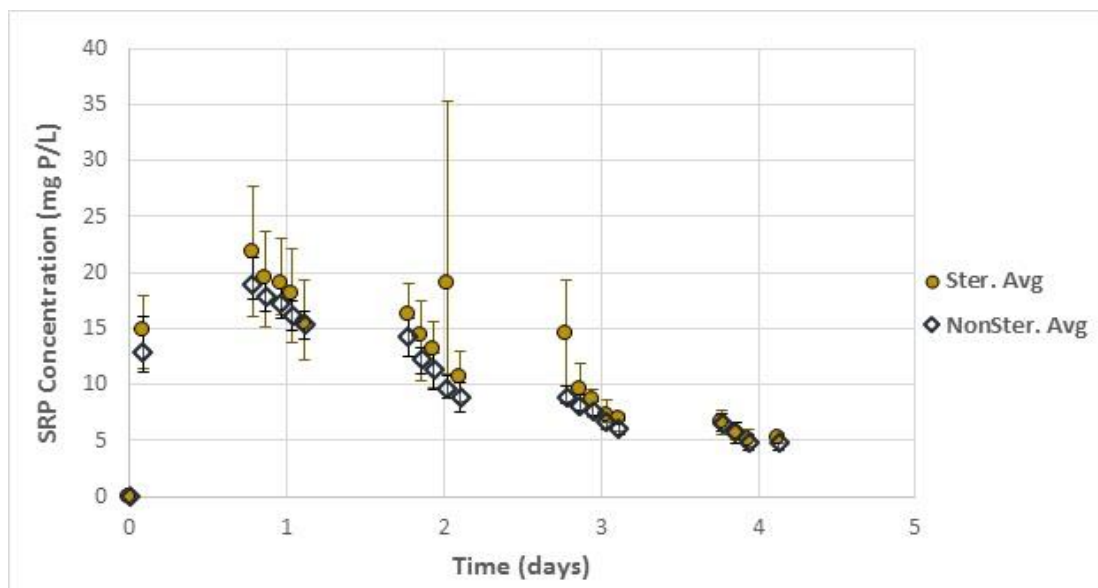


Figure 4.5: The average SRP concentrations of the three sterilized and non-sterilized wood-chip replicates. The error bars represent the range of the SRP concentrations from the three replicates.

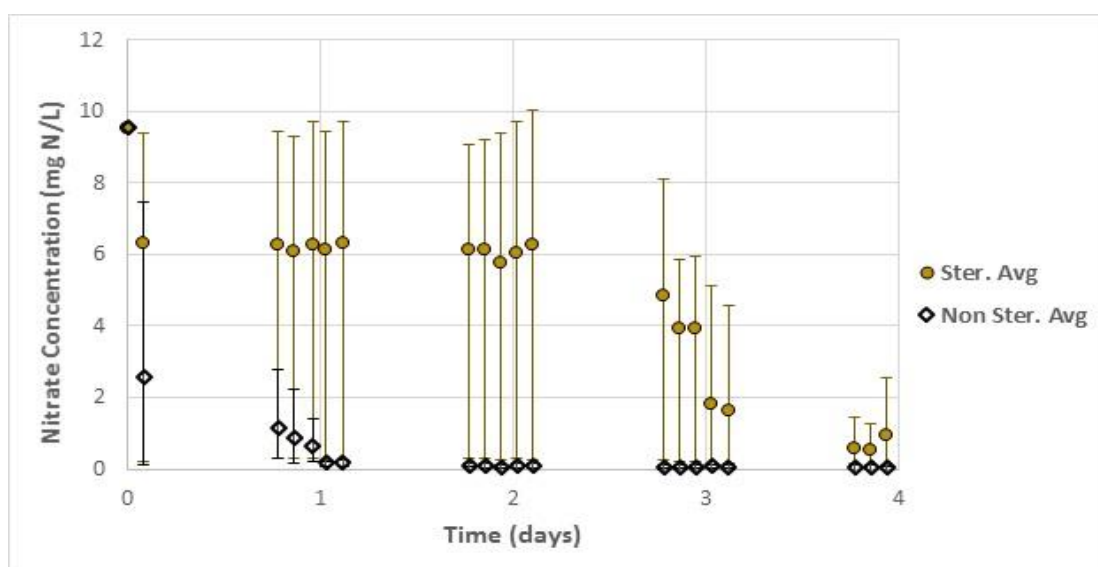


Figure 4.6: The average nitrate concentration of the sterilized and non-sterilized wood-chip replicates. The error bars represent the range of the nitrate concentrations from the three replicates.

Table 4.2: The average maximum and final SRP concentration of the three sterilized and three non-sterilized replicates along with the initial and average final nitrate concentration.

	<b>Average Maximum SRP Conc. (mg P/L)</b>	<b>Average Final SRP Conc. (mg P/L)</b>	<b>Initial NO<sub>3</sub><sup>-</sup> Conc. (mg N/L)</b>	<b>Average Final NO<sub>3</sub><sup>-</sup> Conc. (mg N/L)</b>
<b>Sterilized</b>	21.8	5.3	9.6	0.7
<b>Non-sterilized</b>	18.9	4.8	9.6	0

For all three tests with the wood-chips it was found that the SRP concentration of the effluent increased initially. Two of the three tests eventually started to show a decrease in the SRP concentration with time. This is similar to the results seen in Bell et al. (2015) and Fenton et al. (2016). The TPAC bioreactor in Chichlowski (2014) also observed initial increases in SRP concentration going from the influent to the effluent. Over time the difference in the SRP concentration between the effluent and the influent decreased (Table 4.3).

Table 4.3: The influent and effluent SRP concentration of samples taken from the bioreactor at TPAC (Chichlowski, 2014).

Date	Influent SRP Conc. (mg P/L)	Effluent SRP Conc. (mg P/L)
1/11/2013	0.02	11.76
1/16/2013	0.01	2.06
1/25/2013	0.01	5.52
1/30/2013	0.02	1.73
2/6/2013	0.01	2.30
2/13/2013	0.02	2.45
2/27/2013	0.01	0.75
3/20/2013	0.02	1.01
3/29/2013	0.05	2.55
4/11/2013	0.16	1.46
2/21/2014	0.03	0.18
4/3/2014	0.01	0.15
4/9/2014	0.00	0.07
5/13/2014	0.01	0.20
5/14/2014	0.00	0.19
5/19/2014	0.01	0.03
5/21/2014	0.00	0.03
4/20/2015	0.00	0.02
6/1/2015	0.00	0.03
6/8/2015	0.03	0.05
6/9/2015		0.02
6/22/2015	0.01	0.01
7/2/2015	0.01	0.02
7/15/2015	0.11	0.04
4/11/2016	0.00	0.00
4/12/2016	0.00	0.00
5/2/2016	0.00	0.00
5/3/2016	0.00	0.00

#### 4.4 Bauxite Test Results

Three bauxite disks modified to be at different pH levels were placed in a 2 mg P/L phosphate solution. All three bauxite disks absorbed the phosphorus in the solution. However, each disk exhibited a different SRP absorption rate. Compared to the bauxite



disk of pH 5, the bauxite disks of pH 7 and pH 9 lowered the SRP concentration of the phosphate solution more rapidly. However, after decreasing to a concentration close to 0 mg P/L, the phosphate concentration in the overlying solution slightly increased for pH 7 and pH 9 bauxite disks. At the end of the two-week experiment, all three disks absorbed at least 90% of the SRP in the solution (Figure 4.7). The results of the experiment are summarized in Table 4.4. The mass of phosphorus absorbed by the bauxite disks was determined using the SRP concentration and the volume of the samples and the solution in the beaker before and after sampling. It was determined that the pH 5 bauxite disk absorbed 0.42 mg P, pH 7 bauxite disk absorbed 0.42 mg P and pH 9 bauxite disk absorbed 0.41 mg P giving an average absorption of 0.42 mg P. The SRP reductions seen from the differing pH bauxite disks (93-99%) are larger than those reported in Wang et al. (2010) (27-55%) as well as Ward and Summers (1993) (70%).

A two sample equal variance t-test was performed in Excel to determine if the SRP concentrations were significantly different from one another. All the concentrations, excluding the initial values, for one disk were inputted as Variable 1 and all the concentrations for a second disk were inputted as Variable 2. This test was done three times so that each possible combination of the disks was tested. The results from the t-test indicate that in the range of 5-9 the pH of the bauxite disks does not have a significant effect on phosphorus absorption.

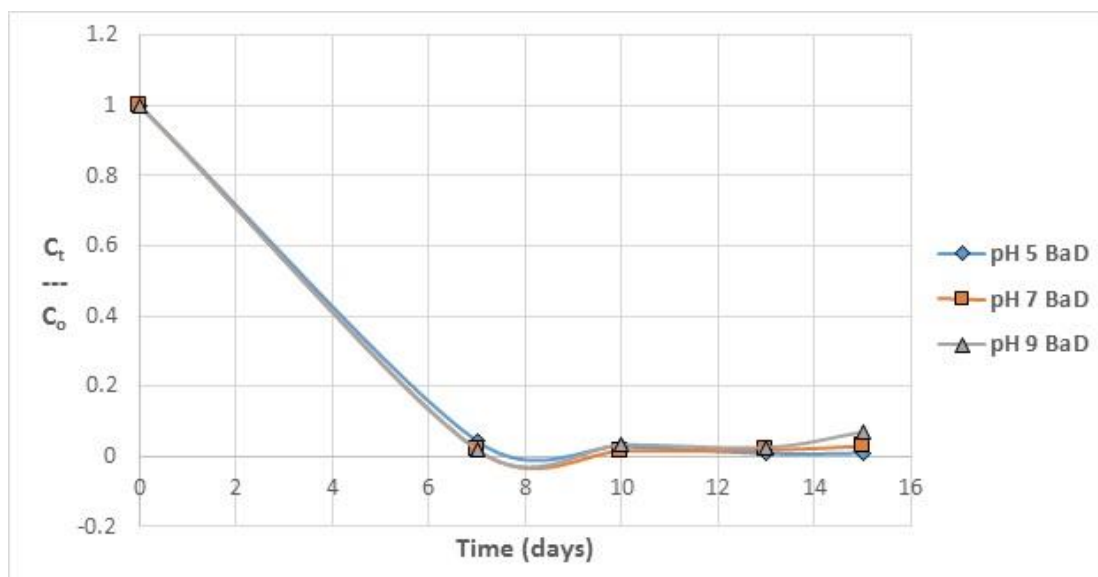


Figure 4.7: The reduction in SRP concentration of the phosphate solution by each altered pH bauxite disk. The y-axis represents the portion of the original SRP that remains in the solution at the time with 1 representing 100%.

Table 4.4: The final SRP concentrations and percent of SRP from the solution that was absorbed by each altered pH bauxite disk.

	Initial SRP Conc. (mg P/L)	Final SRP Conc. (mg P/L)	SRP Absorbed (%)
<b>pH 5</b>	2	0.02	99
<b>pH 7</b>	2	0.06	97
<b>pH 9</b>	2	0.14	93

A 24-hour experiment using three bauxite disks with varying amounts of NaCl (salt), resulted in all three bauxite disks lowering the SRP concentration of the solution (Figure 4.8). The results of the experiment are summarized in Table 4.5. As previously mentioned in Chapter 3, the purpose behind adding NaCl to the bauxite residue is so that

the NaCl will dissolve out of the bauxite disks when they are submerged in water giving more pore space and thus increasing the surface area available for phosphorus sorption. It was hypothesized that the greater the surface area of the disk the more phosphorus the disk would be able to absorb. The bauxite disk labeled 5 reduced the concentration of SRP to 0.2 mg P / L from its initial concentration of 2.1 mg P/L representing a 90% reduction in the overlying water column P concentration. The bauxite disk labeled 3 reduced the initial concentration of 2.2 mg P / L to 0.5 mg P / L or by approximately 75%. The final bauxite disk labeled 1, reduced the SRP concentration from 2.2 mg P / L to 0.7 mg P / L. The SRP solution of Bauxite Disk 1 had a different trend from the other two disks. The SRP concentration dropped to 0.4 mg P/L after 21 hours, but increased back to 0.7 mg P/L until the end of the experiment. Based on the last measured concentration, bauxite disk 1 absorbed about 70% of the SRP in the solution (Figure 4.8). The mass of phosphorus absorbed by the bauxite disks was determined using the SRP concentration and the volume of the samples and the solution in the beaker before and after sampling. It was determined that Bauxite Disk 1 absorbed 0.40 mg P, Bauxite Disk 3 absorbed 0.36 mg P and Bauxite Disk 5 absorbed 0.41 mg P giving an average absorption of 0.39 mg P. Similar to the pH disks, the SRP reductions seen from the differing %NaCl bauxite disks (70-91%) are to SRP reductions reported in Ward and Summers (1993) (70%).

To determine if the SRP concentrations between the different bauxite disks were significantly different from one another, a two-sample equal variance t-test was performed on the data. The same t-test method as the one performed on the pH bauxite

disk concentrations was used. The t-test indicated that the various amounts of NaCl in the bauxite disks did not have a significantly different effect on phosphorus absorption.

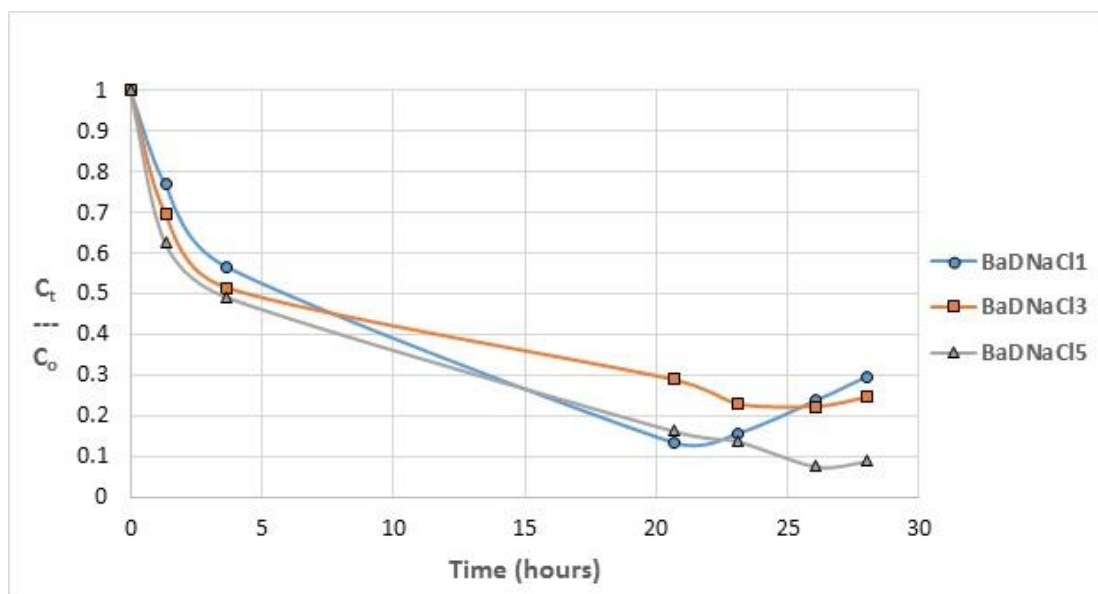


Figure 4.8: The reduction in SRP concentration of the phosphate solution by each NaCl bauxite disk. The y-axis represents the portion of the original SRP that remains in the solution at the time with 1 representing 100%.

Table 4.5: The final SRP concentrations and percent of SRP from the solution that was absorbed by each NaCl bauxite disk.

	Initial SRP Conc. (mg P/L)	Final SRP Conc. (mg P/L)	SRP Absorbed (%)
<b>Bauxite Disk 1</b>	2.2	0.7	70
<b>Bauxite Disk 3</b>	2.2	0.5	75
<b>Bauxite Disk 5</b>	2.1	0.2	91

#### 4.5 One-hour SRP Absorption Test

To better understand how rapidly the bauxite disk could absorb phosphorus a one-hour SRP absorption test was performed. The phosphate solution for the one-hour bauxite test started with a SRP concentration of 2.1 mg P / L. Within the first two minutes of the experiment, the SRP concentration decreased to 1.6 mg P / L, which is a reduction of 24%. A 24% reduction in SRP concentration is close to the 27-55% reduction reported in Wang et al. (2010). The SRP concentration remained around this concentration for the remainder of the experiment (Figure 4.9). The mass loss of phosphorus from the solution is due to absorption by the bauxite disk or extraction from sampling. When observing the mass loss of phosphorus, Figure 4.10 exhibits a linear trend for the phosphorus mass after the SRP concentration levels off. The samples were taken in two minute intervals and were the same volume for forty-two minutes of the test. Based on the results of this experiment it appears that the majority of the phosphorus mass decrease is due to sampling rather than from absorption by the bauxite disk. This could be due to the bauxite disk surface becoming saturated with phosphorus from the fast P sorption reaction within the first two minutes of the experiment while the slow P sorption reaction required more time to absorb the phosphorus into the bauxite disk.

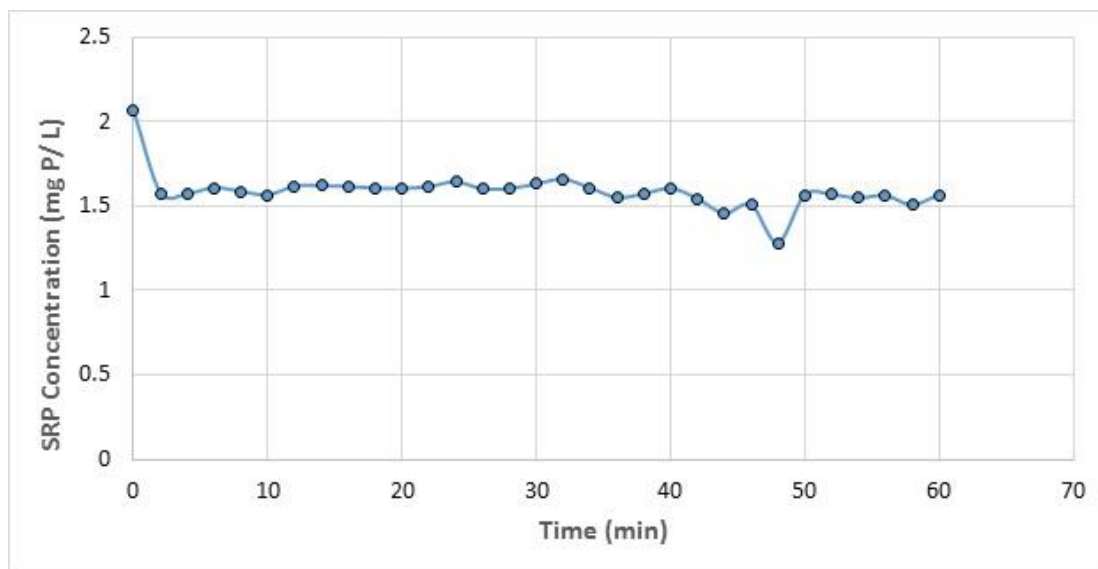


Figure 4.9: The SRP concentration of the phosphate solution that the bauxite was placed in over the course of the experiment.

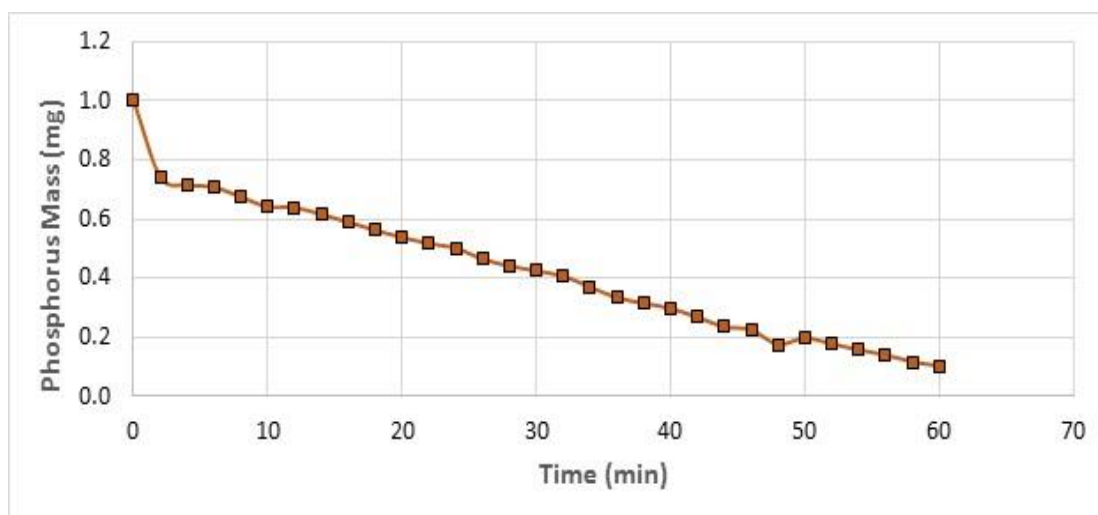


Figure 4.10: The mass of phosphorus in the phosphate solution over the course of the experiment.

#### 4.6 Lab-scale Outflow Box with Bauxite

For this experiment, the phosphate solution initially started at ~2 mg P/L for the 1% NaCl bauxite disk. Two minutes after the bauxite disk was suspended in the box, the SRP concentration of the effluent decreased by about 0.1 mg P/L (Figure 4.11). The 5% SRP reduction observed in this test is much lower than the reductions reported in Wang et al. (2010) as well as Ward and Summers (1993). The effluent remained at this concentration for 1.5 hours. After 1.5 hours the concentration of the water increased back to its initial concentration. This would indicate that the bauxite was no longer absorbing the phosphorus from the water. Since there was not a large change in the SRP concentration throughout the whole experiment, it is likely that the contact time between inflow water and bauxite disk was not long enough for any appreciable absorption to occur or the bauxite disks were quickly saturated with phosphorus.

It has been observed from the previous beaker tests with the bauxite disks that they can absorb about 0.4 mg of phosphorus. To determine if the bauxite disks were possibly becoming saturated with phosphorus the change in SRP concentration seen in the effluent (0.1 mg P/L) was multiplied by the pump flow rate (13.25 L/h) which was then multiplied by the time of sampling. It was estimated that at 15 minutes the mass of phosphorus absorbed by the bauxite would be 0.33 mg P. Assuming that the bauxite disks become saturated with P after absorbing 0.4 mg P, the calculation done above indicates that the bauxite disk most likely became saturated with phosphorus.

The results from this experiment indicated that the bauxite disk could not absorb an appreciable amount of phosphorus from the flowing water to show a large change in SRP

concentration. Phosphorus sorption has two steps: a fast reaction that occurs on the surface of the solid and a slow reaction that occurs inside the solid (Reddy et al., 2005). These two reactions of P sorption could explain why the bauxite was not absorbing enough P to cause a large change in the SRP concentration of the effluent. The bauxite disk could possibly have acquired all the P that it could from the fast reaction within the first 90 minutes of the experiment, but it needed more time for the slow reaction to absorb the P on the surface into the solid. Depending on the rate of the slow reaction, however, it is likely that there would not be a very visible change in the SRP concentration of the effluent.

Since a change of only 0.1 mg P/L was detected in the SRP concentrations from the 1% NaCl disk, the concentration of the stock solution was lowered. It was assumed that by lowering the SRP concentration of the solution a decrease in SRP might be observable. For the run with the 5% NaCl bauxite disk, the solution initially started out with a concentration ~ 0.5 mg P/L. After the bauxite was introduced, the outflow saw a slight increase in the SRP concentration, but after ten minutes the concentration decreased to 0.4 mg P/L (Figure 4.11). This concentration was maintained until 90 minutes into the experiment. It was around this time that the SRP concentration increased. Additionally, the effluent from the run using the 5% NaCl disk experienced slightly more change than the effluent from the run using the 1% NaCl disk, but overall had a relatively constant SRP concentration. In spite of the salt content differences between the disks and the initial SRP concentrations of the flowing water, both disks appeared to stop affecting the concentration of the water at around 90 minutes. Lowering



the flow rate was considered, but the pump used in this experiment was the lowest flowing pump that could be found and used in this experiment.

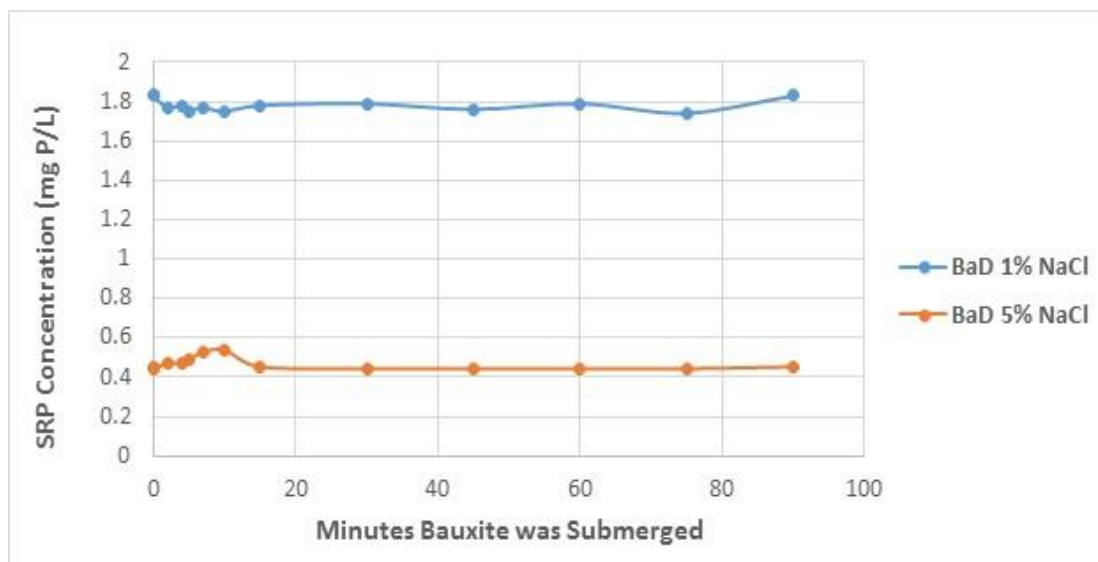


Figure 4.11: The SRP concentration of the lab-scale outflow box effluent over the time that the bauxite disks were suspended in the water.

## CHAPTER 5. SUMMARY AND CONCLUSION

Wood-chip bioreactors have been shown to effectively remove nitrate from influent tile-drain water. However, previous studies have indicated that wood-chip bioreactors may increase concentration of soluble reactive phosphorus in the effluent water. The goals of this research were to (1) better understand the processes affecting SRP release from a bioreactor using benchtop experiments in a controlled environment, and (2) evaluate a potential remediation to the problem using bauxite residue. To understand the increase in phosphorus that was observed in the field bioreactor, three anaerobic water columns were constructed using the same wood-chips as those used in a field bioreactor. Water samples taken from the overlying water columns under anaerobic conditions had maximum SRP concentration ranging from 0.2 – 4.5 mg P/L. Since the water solution used in the anaerobic tests did not contain any P, the phosphorous observed in the samples was being released from the wood-chips.

Upon disassembly of the water columns, a fungus was discovered growing in two of the three water columns. A qualitative correlation could be made when comparing the SRP concentration of each water column with the observable amount of fungus in the respective columns. The column with the highest concentrations of SRP also had the most visible amount of fungus. To determine if the SRP concentration was affected by

the fungal growth, two tests were performed. One test was an aerobic degradation test and the other test was an anaerobic comparison between non-sterilized and sterilized wood-chips.

For the aerobic degradation test, wood-chips from the anaerobic water columns were used to create three jar replicates for each column. The jars were placed on an orbital shaker table to keep them aerobic. An increase in the SRP concentration was observed for all nine jar replicates. The increase in SRP concentration indicated that the release of phosphorus was not dependent on anaerobic conditions and could potentially be caused by the fungus.

Comparing non-sterilized wood-chips with sterilized wood-chips was used to determine if the fungal growth in the columns affects the release of phosphorus from the wood-chips. Three replicates for each type of wood-chip were constructed using the same wood-chips as those used in the field bioreactor. The results from the experiment indicated that the SRP concentrations in the non-sterilized wood-chip jars were not significantly different from the SRP concentrations of the sterilized wood-chip jars. Since there was no significant difference between the sterilized and non-sterilized wood-chips it can be assumed that the fungus does not affect the release of phosphorus from the wood-chips under anaerobic conditions. The phosphorus seen in the outflow of the field bioreactor is a natural product of the decomposition of the wood-chips.

To reduce the loss of phosphorus from the bioreactor effluent, bauxite residue that was pressed and sintered into a solid disk was tested as a possible remediation. Bauxite residue has a hydraulic conductivity that is low enough to potentially cause a blockage in

the tile drain. To increase the hydraulic conductivity of the bauxite residue, the disks were made more porous by adding extra materials to the bauxite residue that would later be removed. After testing different variations of bauxite disks it was observed that making the disks too porous compromised the structural integrity of the bauxite. However, the bauxite disks that were not porous would not allow water to flow through them. It can be concluded that if the bauxite disks were to be used as a remediation then water must be allowed to go around the bauxite disk and not forced to flow through it.

The ability of the bauxite disks to absorb phosphorus from the water was subsequently tested. Three bauxite disks with different pH levels were used. After two weeks it was observed that all three bauxite disks reduced the SRP concentration of the solution by at least 90%. A t-test showed that the SRP concentrations among the different pH disks were not significantly different. It was concluded that, in the range from 5-9, the pH of the bauxite did not significantly affect its ability to absorb phosphorus.

A similar test to the pH bauxite test was done using three bauxite disks with different salt concentrations. The test was performed over a 28-hour period in which each bauxite disk absorbed at least 70% of the initial SRP that was in the solution. Even though one bauxite disk lowered the SRP concentration of the solution more than the other two disks, SRP concentrations were not significantly different among the three bauxite disks.

To understand how rapidly the bauxite disks were absorbing phosphorus, a 1-hour test was performed using a 3% salt mix bauxite disk. Within two minutes the bauxite disk had lowered the SRP concentration of the solution by approximately 0.5 mg P/L. However, the SRP concentration of the solution did not decrease further for the

remainder of the experiment. A possible reason for the SRP concentration of the solution not decreasing any further was that the fast P sorption reaction adsorbed the maximum amount of P that the surface of the bauxite could hold while the slow P sorption reaction needed more time to absorb the P into the bauxite.

A scaled down version of the field outflow box was designed for only one bauxite disk to evaluate its ability to reduce phosphorus from the outflow box of a bioreactor in a bench-top setup. The bauxite disk was suspended in the water filled box and samples were taken from the effluent. Two different attempts were performed with this test using two different bauxite disks and solutions with different initial SRP concentrations. Starting with a 1% NaCl disk and a 2 mg P/L supply solution, it was observed that almost no change in the SRP concentration of the effluent occurred. A slight decrease in the SRP concentration of the effluent occurred within the first ten minutes of the experiment. After the initial decrease the SRP concentration remained similar to the initial SRP concentration. Due to only a 5% reduction in the SRP concentration of the effluent using a 1% NaCl bauxite disk, the SRP concentration of the supply solution was decreased for the second run. A 5% NaCl disk was used with a 0.5 mg P/L supply solution for the second run of the experiment. The 5% NaCl bauxite disk run resulted in a decrease in the SRP concentration of the effluent. However, the SRP concentration did not decrease by a substantial amount and returned to the initial SRP concentration within 90 minutes. The lack of change in the SRP concentration of the effluent is possibly due to the fast and slow P sorption reactions of the bauxite disk. Previous tests of the bauxite disks had the disks sitting in a limited volume of water with a limited supply of phosphorus. The SRP

solution was exposed to the bauxite disk for a relatively longer period of time for two of the tests and only an hour for the third test. The two tests with longer durations resulted in SRP concentration reductions of over 70%. The test that had a duration of one hour, however, resulted in an SRP concentration reduction of 24%. The 24% reduction in the one-hour test was most likely due to the surface of the bauxite disk becoming saturated with phosphorus from the P sorption fast reaction while the slow reaction of P sorption needed more time to absorb the phosphorus into the bauxite disk. This is possibly the same reason why there isn't much of a change in the SRP concentration of the effluent for both runs of the outflow box test. It's possible that if the test was run for a longer duration a larger change in the SRP concentration of the effluent could be observed. Depending on the rate of the slow reaction, however, it is possible that there would not be a very visible change in the SRP concentration of the effluent since the outflow box test had a limitless supply of SRP solution that was flowing over the bauxite disk.

In conclusion, it is uncertain whether using solid bauxite disks to remediate the phosphorus in the effluent of the field bioreactor would be very effective. More testing needs to be conducted to truly understand the limits of solid bauxite for reducing phosphorus losses.

Future work should consist of testing the bauxite disks under different hydraulic retention times (HRTs) for longer durations to better understand the slow P sorption reaction of the bauxite. The use of multiple disks in a lab-scale outflow box at one time should also be tested to determine the mass of bauxite that would be needed in a field

outflow box. Determining the most efficient shape for the bauxite could also help to counter act the slow P sorption reaction of the bauxite.

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## APPENDICES

## Appendix A Anaerobic Water Column Data

Table A.1: Nitrate-N (NO<sub>3</sub>-N) concentration data collected from each of the three anaerobic water columns.

Date	Time	AM/PM	Nitrate Concentrations (mg N/L)		
			Water Column 1	Water Column 2	Water Column 3
9/19/2014		AM	0.23	0.068	0.12
		PM	0.18	0.076	0.14
9/21/2014	11:25	AM	0.19		0.19
	4:47	PM	0.15		0.18
9/22/2014	11:50	AM	0.16	0.08	0.14
	3:57	PM	0.18	0.066	0.15
9/23/2014	10:36	AM		0.071	0.13
	4:57	PM		0.088	0.11
9/24/2014	10:36	AM		0.11	0.10
	5:20	PM		0.092	0.14
9/26/2014	10:47	AM		0.077	0.066
	3:40	PM		0.091	0.096
9/27/2014	10:55	AM		0.11	0.099
	5:48	PM		0.078	0.086
9/29/2014	9:33	AM		0.069	0.064
	5:27	PM		0.069	0.056
9/30/2014	10:33	AM		0.05	0.048
	4:30	PM		0.049	0.081
10/01/2014	10:42	AM		0	0.02
	6:25	PM		0	0.038
10/02/2014	10:20	AM		0	0.024
	5:34	PM		0.001	0.019
10/03/2014	11:01	AM	0.065	0	0.034
	4:18	PM		0	0.024
10/06/2014	11:35	AM		0.004	0
	5:10	PM		0.013	0.016
10/09/2014	10:43	AM	0.056	0.041	0
	5:34	PM	0.06	0.007	0.025
10/10/2014	10:58	AM	0.20	0.046	0.041
	4:03	PM	0.16	0.078	0.042
10/11/2014	11:35	AM	0.095	0.051	0.048
10/12/2014	10:17	AM	0.18	0.036	0.032
	3:56	PM	0.18	0.086	0.021



10/13/2014	11:04	AM	0.17	0.065	0.041
	6:17	PM	0.12	0.061	0.033
10/14/2014	8:20	AM	0.13	0.043	0.043
	3:18	PM	0.14	0.043	0
10/15/2014	10:47	AM	0.30	0.05	0.007
	4:29	PM	0.15	0.039	0
10/16/2014	8:05	AM	0.12	0.075	0
	4:45	PM	0.13	0.058	0
10/17/2014	8:30	AM	0.21	0.071	0.006
	3:55	PM	0.14	0.051	0.017
10/18/2014	3:17	PM	0.097	0.015	0.016
10/19/2014	11:15	AM	0.03	0.014	0
	4:30	PM	0.06	0.025	0
10/20/2014	11:10	AM	0.049	0.012	0.031
	4:27	PM	0.032	0.024	
10/21/2014	11:45	AM	0.017	0.027	
	4:15	PM	0	0	
10/22/2014	10:40	AM	0.041	0.009	
	5:43	PM	0.03	0.015	
10/23/2014	11:25	AM	0.024	0.005	
	6:15	PM	0.045	0.009	

Table A.2: Soluble reactive phosphorus (SRP) concentration data for each of the three anaerobic water columns.

Date	Time	AM/PM	SRP Concentrations (mg P/L)		
			Water Column 1	Water Column 2	Water Column 3
9/19/2014		AM	0.10	0.67	0.091
		PM	0.064	0.66	0.067
9/21/2014	11:25	AM	0.061		0.11
	4:47	PM	0.055		0.16
9/22/2014	11:50	AM	0.056	0.86	0.14
	3:57	PM	0.068	1.1	0.16
9/23/2014	10:36	AM		1.2	0.16
	4:57	PM		0.62	0.17
9/24/2014	10:36	AM		1.7	0.20
	5:20	PM		1.6	0.21
9/26/2014	10:47	AM		1.8	0.31
	3:40	PM		1.3	0.25

9/27/2014	10:55	AM		1.8	0.25
	5:48	PM		2.1	0.25
9/29/2014	9:33	AM		2.3	0.20
	5:27	PM		2.9	0.25
9/30/2014	10:33	AM		2.9	0.33
	4:30	PM		2.5	0.32
10/01/2014	10:42	AM		0.72	0.33
	6:25	PM		0.46	0.38
10/02/2014	10:20	AM		0.51	0.43
	5:34	PM		0.45	0.47
10/03/2014	11:01	AM	0.051	0.91	0.48
	4:18	PM		0.76	0.34
10/06/2014	11:35	AM		1.4	0.34
	5:10	PM		1.2	0.56
10/09/2014	10:43	AM	0.084	3.4	0.32
	5:34	PM	0.09	2.6	0.44
10/10/2014	10:58	AM	0.096	3.6	0.42
	4:03	PM	0.093	3.6	0.46
10/11/2014	11:35	AM	0.11	3.7	0.48
10/12/2014	10:17	AM	0.079	4.0	0.23
	3:56	PM	0.081	3.8	0.29
10/13/2014	11:04	AM	0.089	1.1	0.20
	6:17	PM	0.073	3.6	0.19
10/14/2014	8:20	AM	0.065	2.9	0.17
	3:18	PM	0.067	0.62	0.36
10/15/2014	10:47	AM	0.059	4.0	0.24
	4:29	PM	0.055	1.2	0.41
10/16/2014	8:05	AM	0.063	3.9	0.35
	4:45	PM	0.072	4.3	0.16
10/17/2014	8:30	AM	0.059	4.2	0.39
	3:55	PM	0.062	2.2	0.49
10/18/2014	3:17	PM	0.075	4.0	0.35
10/19/2014	11:15	AM	0.079	4.2	0.39
	4:30	PM	0.069	4.2	0.38
10/20/2014	11:10	AM	0.083	4.2	0.36
	4:27	PM	0.17	4.4	
10/21/2014	11:45	AM	0.088	3.9	
	4:15	PM	0.095	4.2	
10/22/2014	10:40	AM	0.084	4.2	
	5:43	PM	0.11	3.7	
10/23/2014	11:25	AM	0.12	4.5	
	6:15	PM	0.095	4.4	

Table A.3: Temperature data for each of the three anaerobic water columns.

Date	Time	AM/PM	Temperature (°C)		
			Water Column 1	Water Column 2	Water Column 3
9/19/2014		AM	21.5	21.5	21.7
		PM	21.5	21.4	21.6
9/21/2014	11:25	AM	20.5	20.4	20.6
	4:47	PM	20.5	20.5	20.7
9/22/2014	11:50	AM	21.0	21.0	21.2
	3:57	PM	21.2	21.2	21.3
9/23/2014	10:36	AM	21.2	21.3	21.4
	4:57	PM	21.1	21.2	21.3
9/24/2014	10:36	AM		21.2	21.3
	5:20	PM		21.0	21.2
9/26/2014	10:47	AM		21.4	21.6
	3:40	PM		21.2	21.4
9/27/2014	10:55	AM		21.3	21.4
	5:48	PM		20.8	21.0
9/29/2014	9:33	AM		20.9	21.1
	5:27	PM		20.8	21.0
9/30/2014	10:33	AM		21.2	21.3
	4:30	PM		21.2	21.4
10/01/2014	10:42	AM		21.3	21.5
	6:25	PM		21.2	21.4
10/02/2014	10:20	AM		21.2	21.3
	5:34	PM		21.4	21.5
10/03/2014	11:01	AM	20.5	21.3	21.4
	4:18	PM		21.6	21.7
10/06/2014	11:35	AM	21.3	21.2	21.4
	5:10	PM	21.3	21.3	21.4
10/09/2014	10:43	AM	21.3	21.3	21.4
	5:34	PM	21.4	21.4	21.6
10/10/2014	10:58	AM	21.3	21.3	21.5
	4:03	PM	21.3	21.3	21.5
10/11/2014	11:35	AM	21.2	21.2	21.4
10/12/2014	10:17	AM	21.2	21.2	21.3
	3:56	PM	21.1	21.1	21.3
10/13/2014	11:04	AM	21.2	21.2	21.4
	6:17	PM	21.9	22.0	22.1
10/14/2014	8:20	AM	21.4	21.5	21.6
	3:18	PM	21.4	21.4	21.5
10/15/2014	10:47	AM	21.5	21.5	21.6

	4:29	PM	21.6	21.6	21.7
10/16/2014	8:05	AM	21.5	21.5	21.7
	4:45	PM	21.6	21.6	21.7
10/17/2014	8:30	AM	21.6	21.6	21.7
	3:55	PM	21.6	21.6	21.7
10/18/2014	3:17	PM	21.2	21.2	21.4
10/19/2014	11:15	AM	21.1	21.1	21.3
	4:30	PM	21.2	21.2	21.3
10/20/2014	11:10	AM	21.4	21.4	21.6
	4:27	PM	21.3	21.4	
10/21/2014	11:45	AM	20.3	20.4	
	4:15	PM	20.7	20.7	
10/22/2014	10:40	AM	20.8	20.8	
	5:43	PM			
10/23/2014	11:25	AM	19.7	19.8	
	6:15	PM	19.6	19.6	

Table A.4: Oxidation-Reduction Potential (ORP) data for each of the three anaerobic water columns.

Date	Time	AM/PM	Oxidation-Reduction Potential (ORP) (mV)		
			Water Column 1	Water Column 2	Water Column 3
9/19/2014		AM	-77.7	-79.8	-390.6
		PM	-123.1	-192.0	-452.4
9/21/2014	11:25	AM	-466.0	-441.5	-413.4
	4:47	PM	-376.7	-456.0	-373.3
9/22/2014	11:50	AM	-268.6	-464.4	-369.8
	3:57	PM	-260.7	-462.4	-370.5
9/23/2014	10:36	AM	-293.2	-450.5	-368.0
	4:57	PM	-296.8	-443.4	-367.8
9/24/2014	10:36	AM		-433.3	-357.5
	5:20	PM		-428.0	-350.9
9/26/2014	10:47	AM		-414.0	-333.3
	3:40	PM		-411.6	-329.8
9/27/2014	10:55	AM		-402.9	-336.3
	5:48	PM		-399.1	-338.8
9/29/2014	9:33	AM		-384.7	-334.1
	5:27	PM		-378.4	-333.2
9/30/2014	10:33	AM		-368.6	-336.3

	4:30	PM		-361.1	-335.3
10/01/2014	10:42	AM		-358.1	-321.5
	6:25	PM		-352.2	-327.2
10/02/2014	10:20	AM		-351.4	-320.4
	5:34	PM		-354.1	-317.1
10/03/2014	11:01	AM	-52.2	-356.0	-324.9
	4:18	PM		-344.8	-324.1
10/06/2014	11:35	AM	-304.3	-344.8	-320.2
	5:10	PM	-317.4	-340.3	-301.6
10/09/2014	10:43	AM	-315.7	-338.4	-305.1
	5:34	PM	-302.4	-338.6	-301.2
10/10/2014	10:58	AM	-302.2	-332.3	-301.7
	4:03	PM	-302.8	-330.7	-301.4
10/11/2014	11:35	AM	-300.9	-329.4	-300.3
10/12/2014	10:17	AM	-299.8	-327.8	-299.4
	3:56	PM	-300.0	-328.9	-300.3
10/13/2014	11:04	AM	-299.9	-334.4	-299.9
	6:17	PM	-285.1	-324.5	-290.2
10/14/2014	8:20	AM	-286.5	-325.4	-291.0
	3:18	PM	-286.2	-323.8	-290.8
10/15/2014	10:47	AM	-286.1	-324.6	-294.3
	4:29	PM	-282.2	-323.1	-291.3
10/16/2014	8:05	AM	-282.9	-325.8	-291.8
	4:45	PM	-282.2	-324.2	-291.6
10/17/2014	8:30	AM	-282.4	-323.4	-292.1
	3:55	PM	-281.2	-323.3	-291.3
10/18/2014	3:17	PM	-280.0	-323.4	-289.3
10/19/2014	11:15	AM	-279.8	-323.5	-289.9
	4:30	PM	-278.2	-320.3	-289.8
10/20/2014	11:10	AM	-277.7	-323.1	-289.1
	4:27	PM	-275.0	-321.6	
10/21/2014	11:45	AM	-272.6	-322.3	
	4:15	PM	-269.3	-320.9	
10/22/2014	10:40	AM	-270.3	-319.7	
	5:43	PM			
10/23/2014	11:25	AM	-268.3	-319.9	
	6:15	PM	-267.7	-318.1	

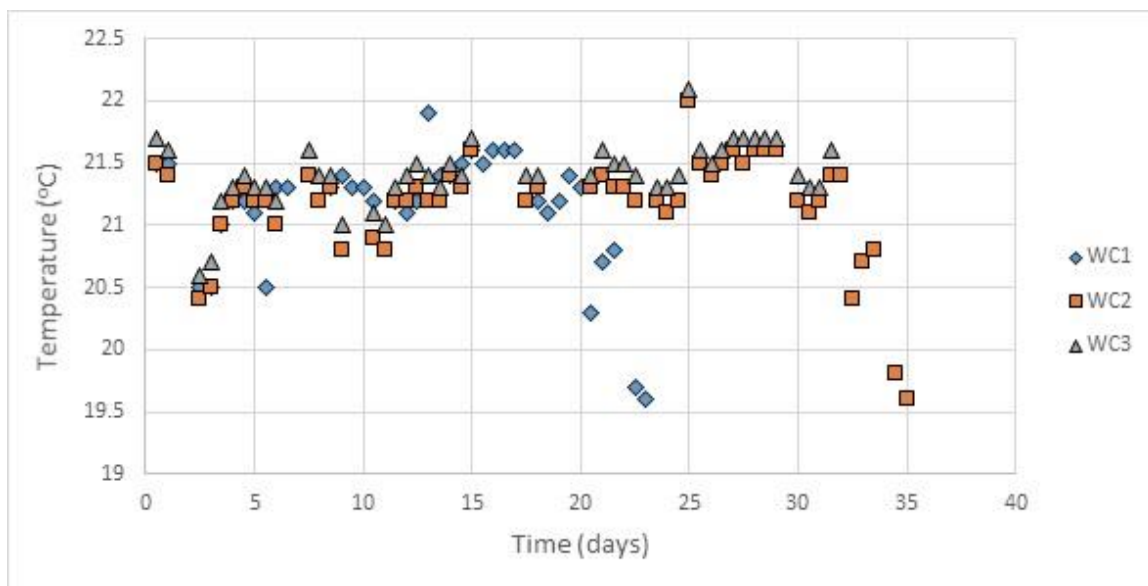


Figure A.1: Temperatures of each anaerobic water column over time.

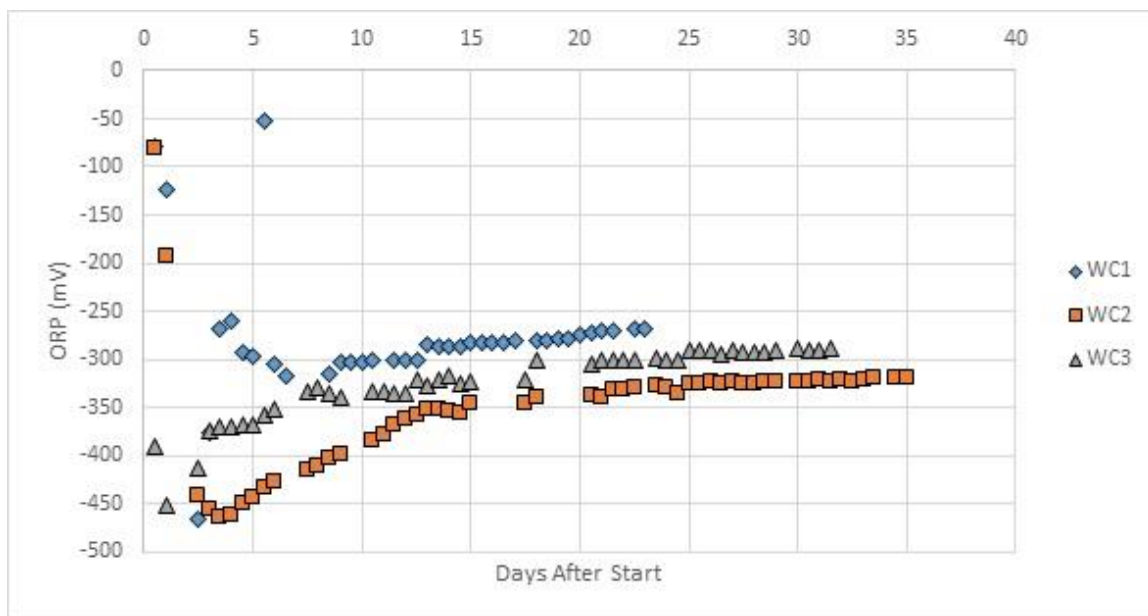


Figure A.2: Oxidation-Reduction Potential levels of each anaerobic water column over time.

## Appendix B    Aerobic Degradation Data

Table B.1: SRP concentration data from the three Water Column 1 replicates and the average SRP concentration of the three replicates.

SRP Concentration (mg P/L)		Water Column 1		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	0.011	0.011	0.011	0.011
3/10/15	0.073	0.08	0.055	0.069
3/11/15 AM	0.074	0.083	0.063	0.073
3/11/15 PM	0.076	0.076	0.053	0.068
3/12/15 AM	0.086	0.25	0.082	0.14
3/12/15 PM	0.12	0.16	0.11	0.13
3/13/15	0.12	0.25	0.20	0.19
3/14/15	0.17	0.18	0.21	0.18
3/15/15	0.14	0.17	0.22	0.18
3/16/15	0.087	0.17	0.19	0.15
3/17/15	0.089	0.085	0.096	0.09
3/18/15	0.063	0.054	0.06	0.059
3/19/15	0.053	0.057	0.049	0.053
3/20/15	0.036	0.046	0.042	0.041
3/21/15	0.037	0.042	0.034	0.038
3/22/15	0.026	0.036	0.033	0.032
3/23/15	0.027	0.031	0.029	0.029
3/24/15	0.022	0.032	0.029	0.028

Table B.2: SRP concentration data from the three Water Column 2 replicates and the average SRP concentration of the three replicates.

SRP Concentration (mg P/L)		Water Column 2		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	0.011	0.011	0.011	0.011
3/10/15	1.5	1.2	0.96	1.2
3/11/15 AM	0.36	0.20	0.12	0.22
3/11/15 PM	0.13	0.1	0.096	0.11
3/12/15 AM	0.16	0.18	0.20	0.18
3/12/15 PM	0.16	0.17	0.18	0.17
3/13/15	0.16	0.18	0.17	0.17

3/14/15	0.40	0.45	0.33	0.39
3/15/15	0.34	0.41	0.61	0.45
3/16/15	0.36	0.35	0.41	0.37
3/17/15	0.27	0.35	0.40	0.34
3/18/15	0.12	0.10	0.096	0.11
3/19/15	0.11	0.10	0.11	0.11
3/20/15	0.069	0.079	0.072	0.073
3/21/15	0.091	0.068	0.059	0.073
3/22/15	0.099	0.072	0.061	0.077
3/23/15	0.094	0.069	0.086	0.083
3/24/15	0.08	0.08	0.07	0.077

Table B.3: SRP concentration data from the three Water Column 3 replicates and the average SRP concentration of the three replicates.

SRP Concentration (mg P/L)		Water Column 3		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	0.011	0.011	0.011	0.011
3/10/15	0.057	0.055	0.054	0.055
3/11/15 AM	0.045	0.041	0.041	0.042
3/11/15 PM	0.062	0.06	0.054	0.059
3/12/15 AM	0.074	0.12	0.23	0.14
3/12/15 PM	0.11	0.10	0.099	0.10
3/13/15	0.098	0.10	0.10	0.10
3/14/15	0.058	0.11	0.11	0.092
3/15/15	0.072	0.057	0.049	0.059
3/16/15	0.064	0.059	0.032	0.052
3/17/15	0.04	0.047	0.036	0.041
3/18/15	0.025	0.031	0.021	0.026
3/19/15	0.022	0.029	0.019	0.023
3/20/15	0.023	0.026	0.018	0.022
3/21/15	0.041	0.027	0.018	0.029
3/22/15	0.021	0.03	0.017	0.023
3/23/15	0.021	0.028	0.017	0.022
3/24/15	0.02	0.032		



Table B.4: Nitrate concentration data from the three Water Column 1 replicates and the average nitrate concentration of the three replicates.

Nitrate Concentration (mg N/L)		Water Column 1		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	8.5	8.5	8.5	8.5
3/10/15	7.7	7.4	7.1	7.4
3/11/15 AM	0.12	0.11	0.20	0.14
3/11/15 PM	0.07	0.10	0.11	0.096
3/12/15 AM	0.12	0.16	0.11	0.13
3/12/15 PM	0.14	0.18	0.13	0.15
3/13/15	0.16	0.24	0.21	0.20
3/14/15	0.14	0.17	0.16	0.16
3/15/15	0.15	0.18	0.20	0.17
3/16/15	0.13	0.14	0.16	0.14
3/17/15	0.14	0.14	0.097	0.13
3/18/15	0.17	0.16	0.17	0.16
3/19/15	0.16	0.15	0.14	0.15
3/20/15	0.14	0.15	0.14	0.14
3/21/15	0.13	0.18	0.13	0.15
3/22/15	0.13	0.16	0.13	0.14
3/23/15	0.15	0.15	0.14	0.15
3/24/15	0.14	0.20	0.14	0.16

Table B.5: Nitrate concentration data from the three Water Column 2 replicates and the average nitrate concentration of the three replicates.

Nitrate Concentration (mg N/L)		Water Column 2		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	8.5	8.5	8.5	8.5
3/10/15	8.3	8.4	7.8	8.2
3/11/15 AM	2.1	0.32	0.91	1.1
3/11/15 PM	0.95	0.13	0.28	0.45
3/12/15 AM	0.74	0.14	0.16	0.35
3/12/15 PM	0.76	0.19	0.22	0.39
3/13/15	0.25	0.21	0.26	0.24
3/14/15	0.14	0.14	0.14	0.14
3/15/15	0.17	0.16	0.12	0.15
3/16/15	0.13	0.13	0.11	0.12
3/17/15	0.12	0.096	0.10	0.11

3/18/15	0.16	0.15	0.16	0.16
3/19/15	0.14	0.15	0.12	0.14
3/20/15	0.15	0.13	0.12	0.13
3/21/15	0.13	0.13	0.13	0.13
3/22/15	0.13	0.13	0.14	0.13
3/23/15	0.13	0.12	0.13	0.12
3/24/15	0.11	0.11	0.10	0.11

Table B.6: Nitrate concentration data from the three Water Column 3 replicates and the average nitrate concentration of the three replicates.

Nitrate Concentration (mg N/L)		Water Column 3		
Date	Replicate 1	Replicate 2	Replicate 3	Average
Initial	8.5	8.5	8.5	8.5
3/10/15	6.9	6.9	7.8	7.2
3/11/15 AM	0.087	0.083	0	0.057
3/11/15 PM	0.099	0.098	0.11	0.10
3/12/15 AM	0.11	0.11	0.095	0.10
3/12/15 PM	0.14	0.13	0.11	0.13
3/13/15	0.18	0.18	0.16	0.17
3/14/15	0.13	0.13	0.12	0.13
3/15/15	0.12	0.13	0.15	0.13
3/16/15	0.13	0.11	0.13	0.12
3/17/15	0.097	0.10	0.092	0.097
3/18/15	0.13	0.13	0.13	0.13
3/19/15	0.1	0.13	0.13	0.12
3/20/15	0.14	0.12	0.11	0.12
3/21/15	0.12	0.13	0.13	0.13
3/22/15	0.13	0.13	0.15	0.14
3/23/15	0.12	0.14	0.15	0.14
3/24/15	0.11	0.098		

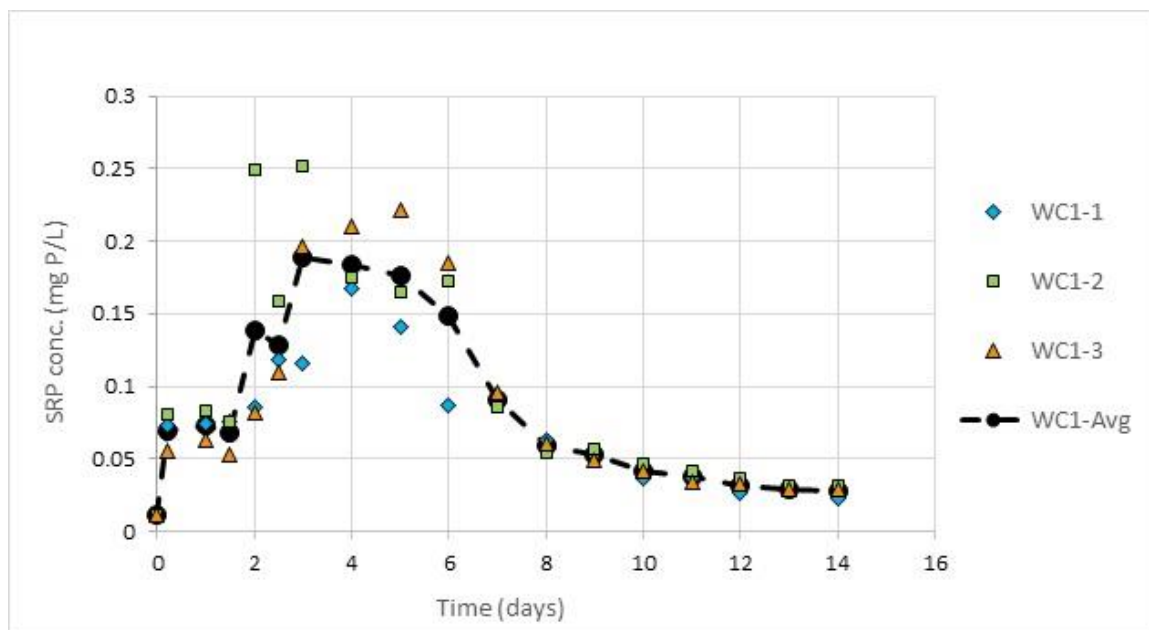


Figure B.1: SRP concentrations of the Water Column 1 replicates and the average of the replicates.

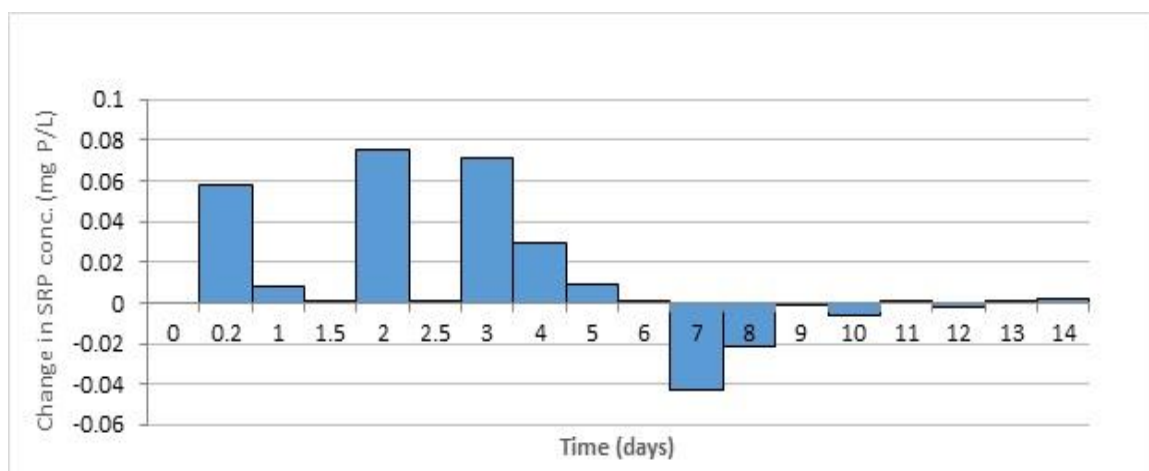


Figure B.2: The average change in the SRP concentration of the Water Column 1 replicates. The change was acquired by subtracting the SRP concentration in the jar after refilling from the SRP concentration of the next sample.

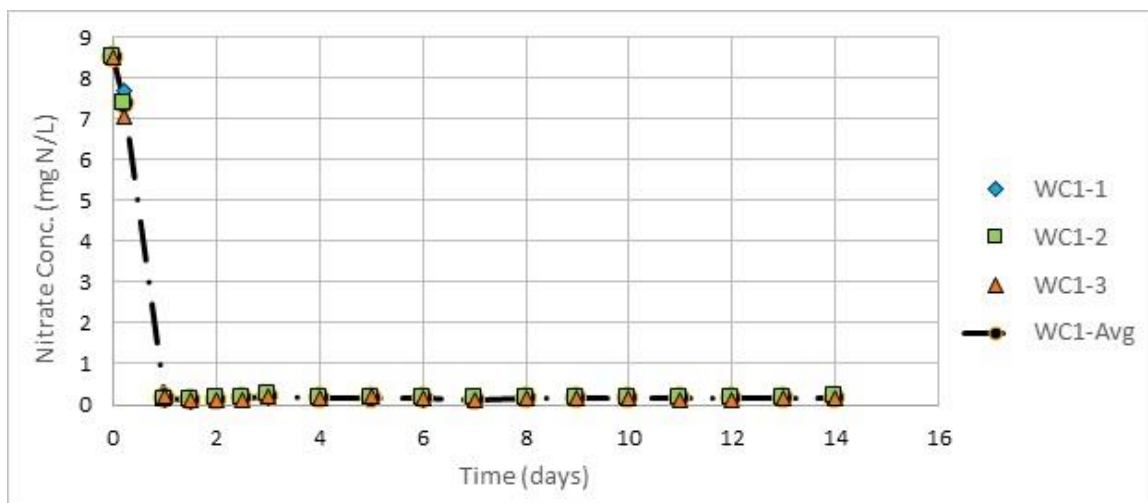


Figure B.3: Nitrate concentrations of the Water Column 1 replicates and the average of the replicates.

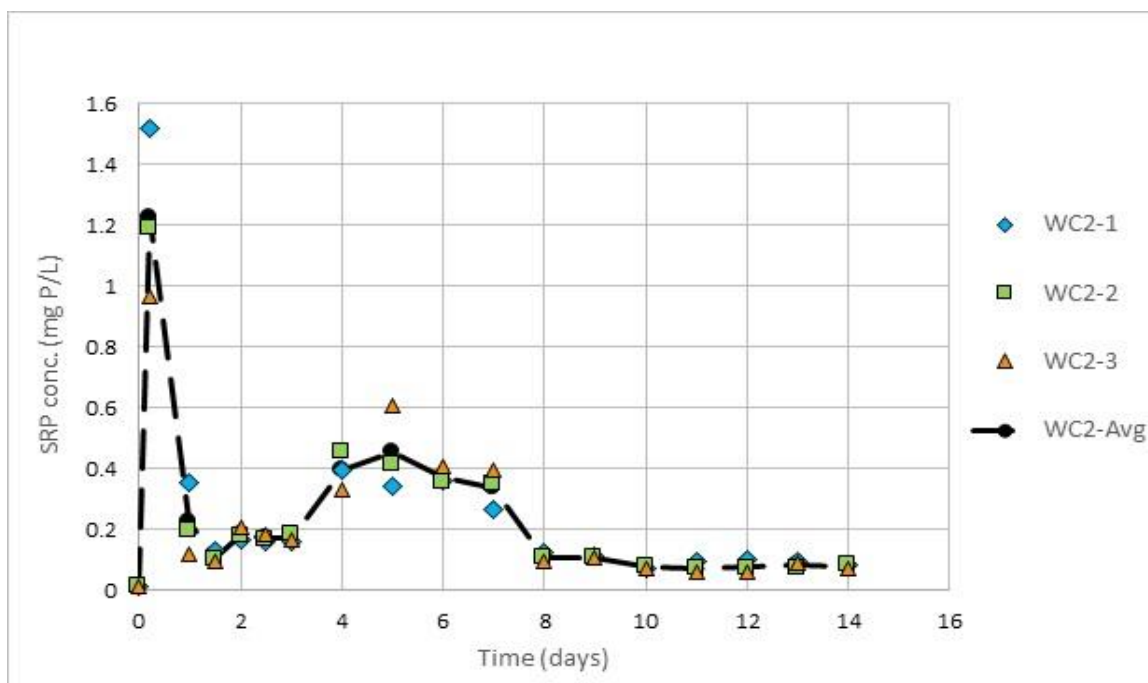


Figure B.4: SRP concentrations of the Water Column 2 replicates and the average of the replicates.

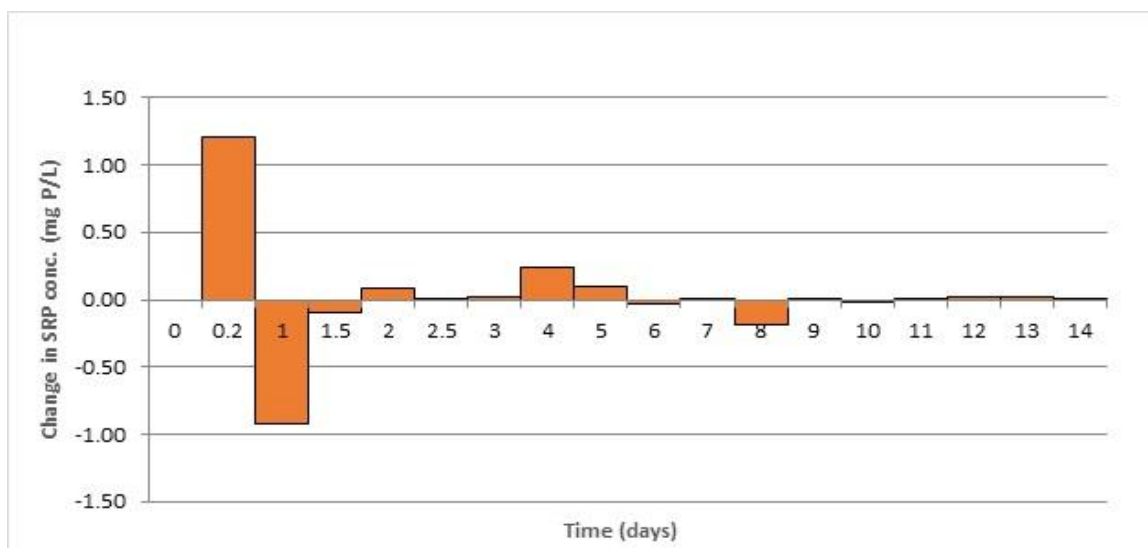


Figure B.5: The average change in the SRP concentration of the Water Column 2 replicates. The change was acquired by subtracting the SRP concentration in the jar after refilling from the SRP concentration of the next sample.

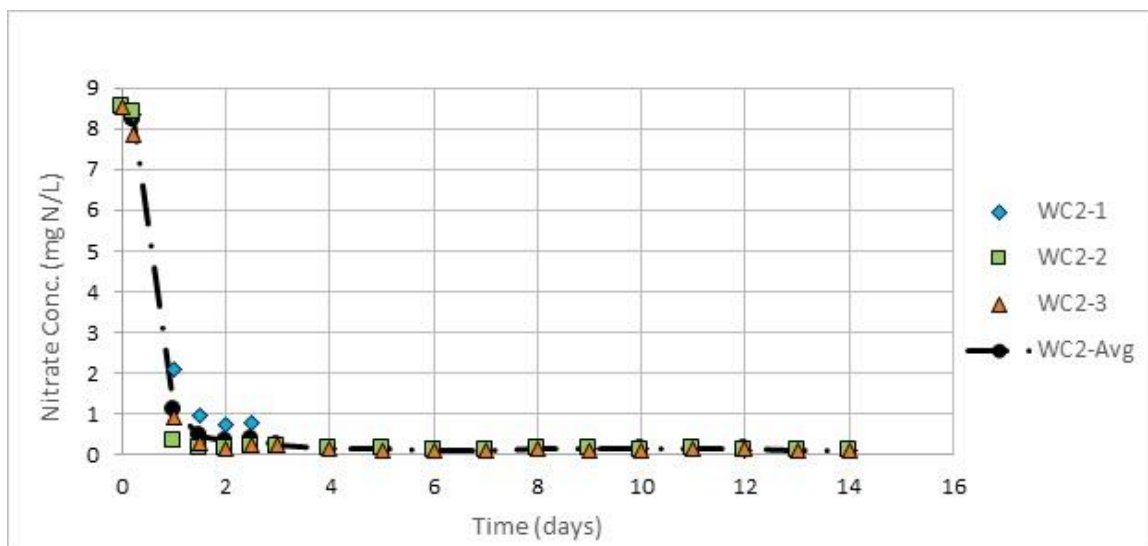


Figure B.6: Nitrate concentrations of the Water Column 2 replicates and the average of the replicates.

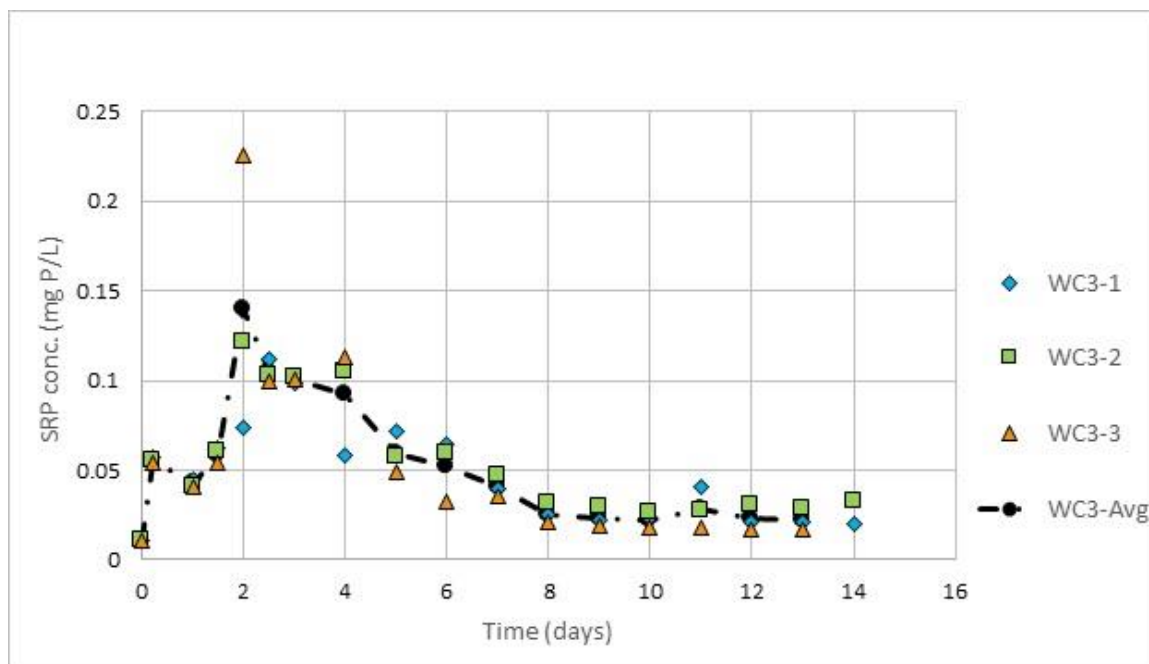


Figure B.7: SRP concentrations of the Water Column 3 replicates and the average of the replicates.

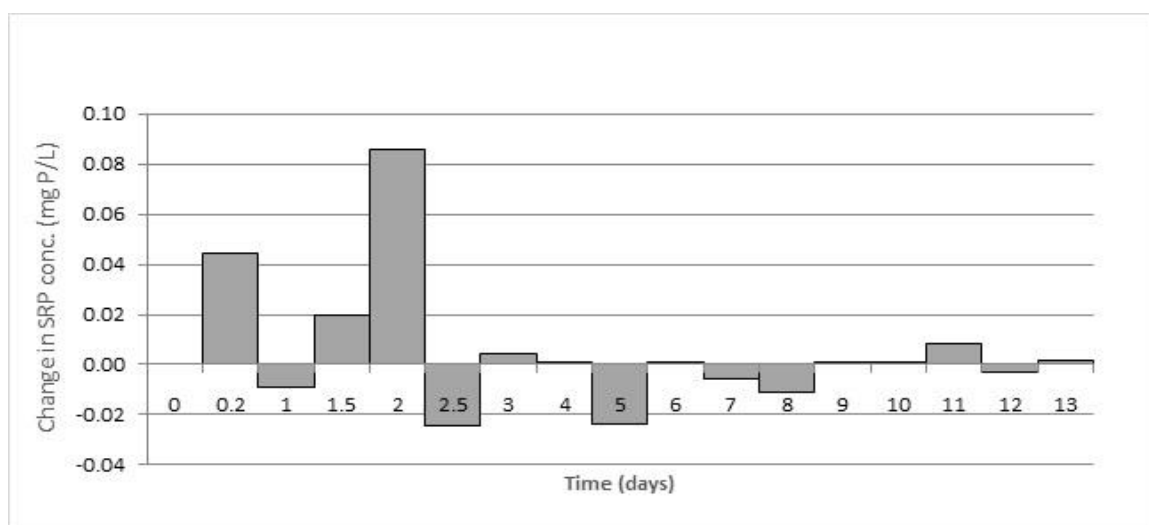


Figure B.8: The average change in the SRP concentration of the Water Column 3 replicates. The change was acquired by subtracting the SRP concentration in the jar after refilling from the SRP concentration of the next sample.

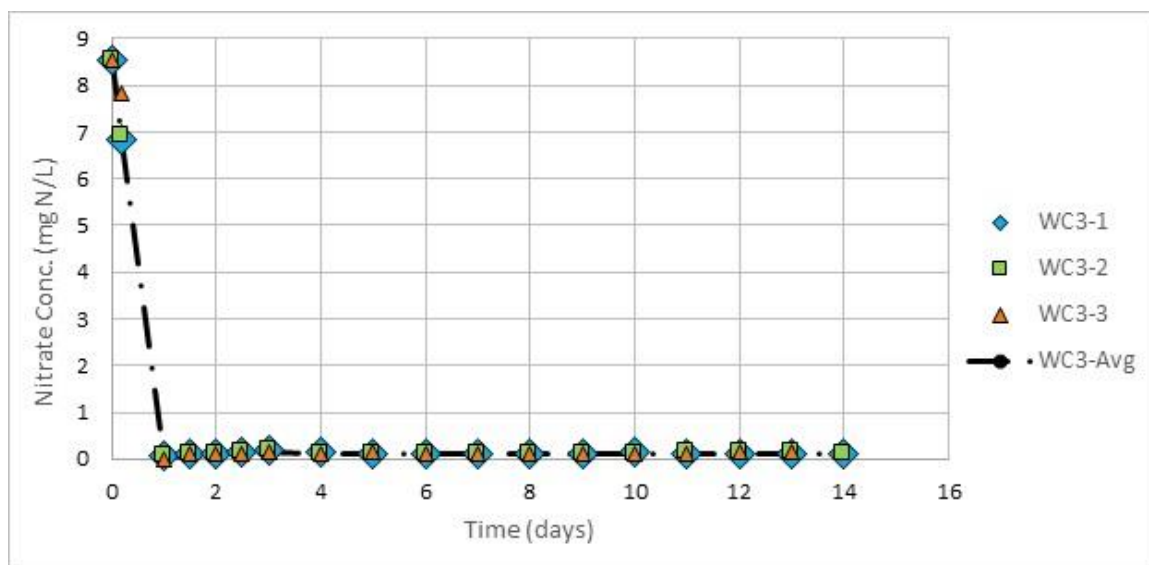


Figure B.9: Nitrate concentrations of the Water Column 3 replicates and the average of the replicates.

## Appendix C Sterilized Wood-chip Data

Table C.1: SRP concentration data from the three sterilized wood-chip replicates and the average SRP concentration of the three replicates.

SRP Concentration (mg P/L)		Sterilized Woodchips			
Date	Time	Replicate 1	Replicate 2	Replicate 3	Average
11/30/2015	13:30	0.018	0.018	0.018	0.018
	15:30	11.5	15.1	18.0	14.9
12/1/2015	8:15	16.1	21.7	27.7	21.8
	10:15	15.2	19.6	23.6	19.5
	12:30	16.2	17.8	23.0	19.0
	14:15	13.7	18.4	22.2	18.1
	16:15	12.2	14.7	19.3	15.4
12/2/2015	8:00	12.6	16.8	19.0	16.1
	10:00	10.3	15.2	17.4	14.3
	12:00	9.6	14.2	15.6	13.1
	14:00	11.0	10.9	35.2	19.0
	16:00	8.5	10.6	13.0	10.7
12/3/2015	8:15	8.4	19.3	15.8	14.5
	10:15	7.5	9.2	12.0	9.6
	12:15	7.1	9.0	9.6	8.6
	14:15	6.6	6.6	8.6	7.3
	16:15	5.8	7.4	7.4	6.9
12/4/2015	8:00	5.5	6.5	7.7	6.5
	10:00	5.5	5.1	6.5	5.7
	12:00	4.4	4.8	6.0	5.1
	16:40	4.7	5.7	5.3	5.3



Table C.2: SRP concentration data from the three non-sterilized wood-chip replicates and the average SRP concentration of the three replicates.

SRP Concentration (mg P/L)		Non-Sterilized Woodchips			
Date	Time	Replicate 1	Replicate 2	Replicate 3	Average
11/30/2015	13:30	0.018	0.018	0.018	0.018
	15:30	11.7	11.0	16.0	12.9
12/1/2015	8:15	17.6	17.8	21.4	18.9
	10:15	17.4	16.5	19.6	17.8
	12:30	15.9	16.6	19.2	17.2
	14:15	16.2	14.9	17.5	16.2
	16:15	15.7	14.0	16.5	15.4
12/2/2015	8:00	12.6	14.3	16.0	14.3
	10:00	11.0	12.6	13.3	12.3
	12:00	9.5	11.5	12.8	11.3
	14:00	8.7	9.2	10.8	9.6
	16:00	7.6	8.8	10.2	8.8
12/3/2015	8:15	8.3	8.4	9.8	8.9
	10:15	7.7	7.7	9.1	8.1
	12:15	7.2	7.3	8.5	7.7
	14:15	6.0	6.7	7.6	6.7
	16:15	5.5	6.0	6.8	6.1
12/4/2015	8:00	5.9	6.4	7.4	6.6
	10:00	4.7	5.8	6.6	5.7
	12:00	4.2	4.9	5.5	4.9
	16:40	4.1	4.9	5.3	4.8

Table C.3: Nitrate concentration data from the three sterilized wood-chip replicates and the average nitrate concentration of the three replicates.

Nitrate Concentration (mg N/L)		Sterilized Woodchips			
Date	Time	Replicate 1	Replicate 2	Replicate 3	Average
11/30/2015	13:30	9.6	9.6	9.6	9.6
	15:30	9.4	9.3	0.21	6.3
12/1/2015	8:15	9.4	9.1	0.28	6.3
	10:15	9.3	8.6	0.31	6.1
	12:30	9.7	8.8	0.28	6.3
	14:15	9.4	8.7	0.25	6.1

	16:15	9.7	9.1	0.25	6.3
12/2/2015	8:00	9.1	9.1	0.32	6.2
	10:00	9.2	9.0	0.28	6.2
	12:00	9.4	7.6	0.27	5.8
	14:00	9.7	8.1	0.29	6.0
	16:00	10.0	8.5	0.26	6.3
12/3/2015	8:15	8.1	6.2	0.26	4.9
	10:15	5.8	5.8	0.19	4.0
	12:15	5.6	6.0	0.20	3.9
	14:15	5.1	0.13	0.19	1.8
	16:15	4.6	0.14	0.16	1.6
12/4/2015	8:00	1.4	0.15	0.16	0.58
	10:00	1.3	0.13	0.16	0.52
	12:00	2.6	0.13	0.13	0.94
	16:40	1.9	0.14	0.13	0.71

Table C.4: Nitrate concentration data from the three non-sterilized wood-chip replicates and the average nitrate concentration of the three replicates.

Nitrate Concentration (mg N/L)		Non-Sterilized Wood-chips			
Date	Time	Replicate 1	Replicate 2	Replicate 3	Average
11/30/2015	13:30	9.6	9.6	9.6	9.6
	15:30	7.5	0.17	0.10	2.6
12/1/2015	8:15	2.8	0.28	0.32	1.1
	10:15	2.2	0.27	0.18	0.89
	12:30	1.4	0.31	0.19	0.64
	14:15	0.09	0.23	0.19	0.17
	16:15	0.08	0.23	0.18	0.17
12/2/2015	8:00	0.047	0.17	0.1	0.11
	10:00	0.041	0.14	0.079	0.087
	12:00	0.041	0.12	0.017	0.061
	14:00	0.04	0.18	0.024	0.082
	16:00	0.032	0.14	0.041	0.072
12/3/2015	8:15	0.035	0.13	0.017	0.060
	10:15	0.053	0.097	0.043	0.064
	12:15	0.021	0.11	0.001	0.044
	14:15	0.018	0.13	0.083	0.077
	16:15	0.014	0.11	0.072	0.064
12/4/2015	8:00	0.0	0.10	0.054	0.042

	10:00	0.0	0.13	0.11	0.069
	12:00	0.0	0.089	0.062	0.040
	16:40	0.0	0.13	0.049	0.049

Table C.5: Temperature data from two of the non-sterilized wood-chip replicates.

Temperature (°C)		Non-Sterilized Wood-chips	
Date	Time	Replicate 1	Replicate 3
11/30/2015	13:30	22.9	22.6
	15:30	22.6	22.5
12/1/2015	8:15	22.4	22.4
	10:15	22.0	21.9
	12:30	21.9	21.8
	14:15	22.0	21.7
	16:15	21.9	21.8
12/2/2015	8:00	22.3	22.4
	10:00	21.7	21.7
	12:00	21.6	21.5
	14:00	21.5	21.4
	16:00	21.6	21.4
12/3/2015	8:15	22.2	22.2
	10:15	21.9	21.9
	12:15	22.0	22.0
	14:15	22.1	21.9
	16:15	22.0	22.0
12/4/2015	8:00	22.4	22.4
	10:00	22.0	21.9
	12:00	21.9	21.7
	16:40	22.1	22.0

Table C.6: Oxidation-Reduction Potential data from two of the non-sterilized wood-chip replicates.

ORP (mV)		Non-Sterilized Wood-chips	
Date	Time	Replicate 1	Replicate 3
11/30/2015	13:30	235.4	192.4
	15:30	229.5	189.2
12/1/2015	8:15	-96.9	-42.3
	10:15	-224.1	-55.9
	12:30	-346.5	-79.0
	14:15	-400.4	-105.0
	16:15	-437.3	-131.6
12/2/2015	8:00	-477.1	-472.0
	10:00	-473.6	-462.9
	12:00	-475.6	-465.4
	14:00	-477.7	-467.8
	16:00	-478.6	-467.7
12/3/2015	8:15	-481.0	-475.1
	10:15	-482.2	-475.1
	12:15	-484.6	-476.1
	14:15	-486.4	-476.2
	16:15	-488.0	-476.6
12/4/2015	8:00	-488.3	-478.7
	10:00	-488.7	-476.3
	12:00	-489.1	-476.2
	16:40	-491.4	-478.3

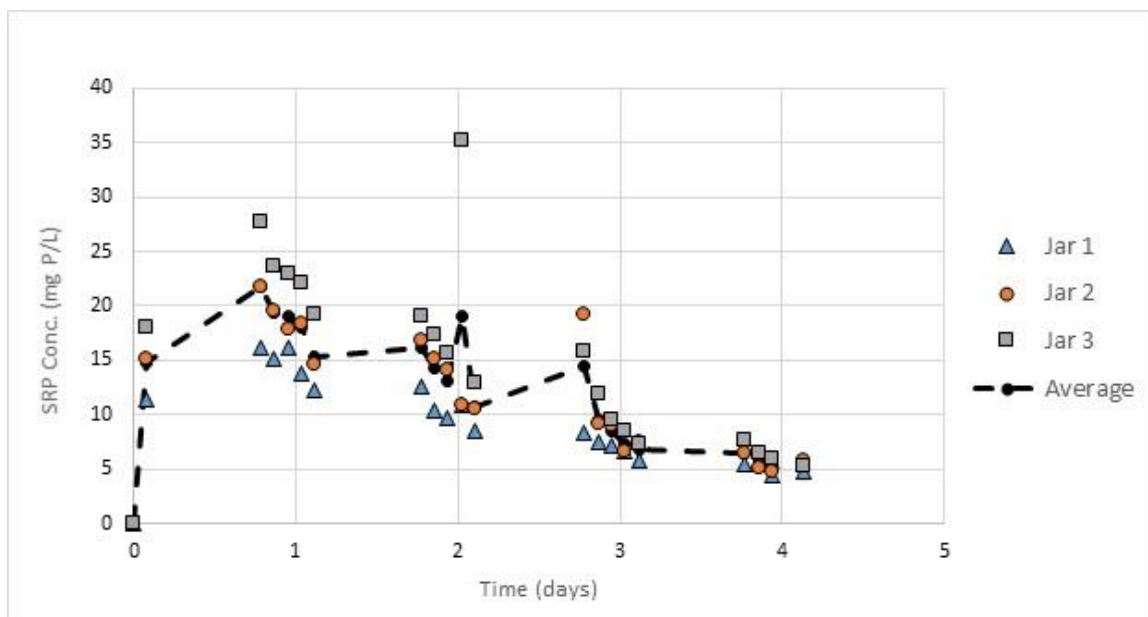


Figure C.1: SRP concentrations of the sterilized wood-chip replicates and the average of the replicates.

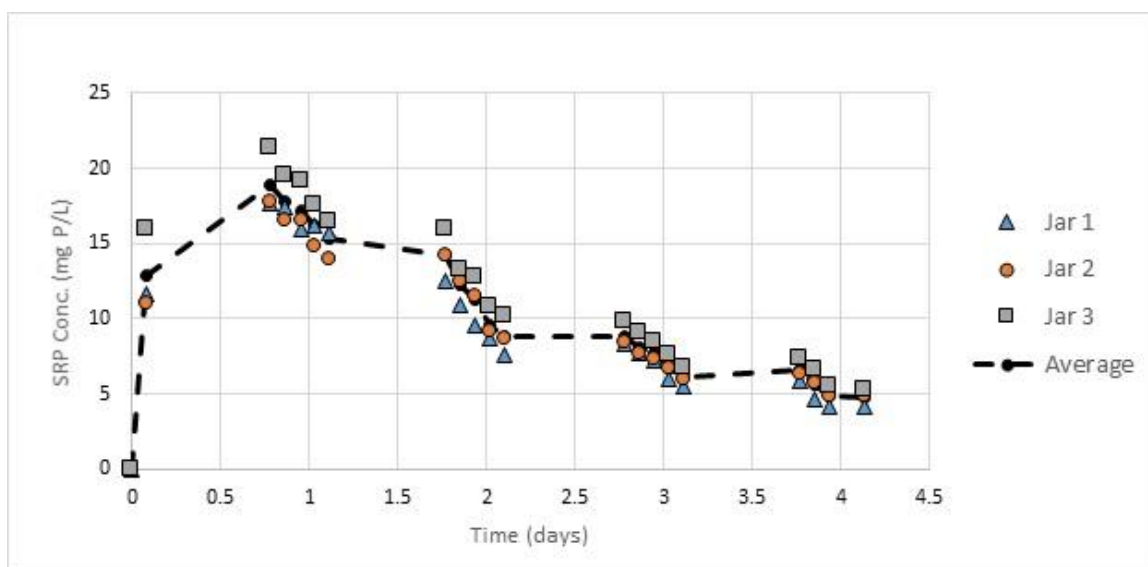


Figure C.2: SRP concentrations of the non-sterilized wood-chip replicates and the average of the replicates.

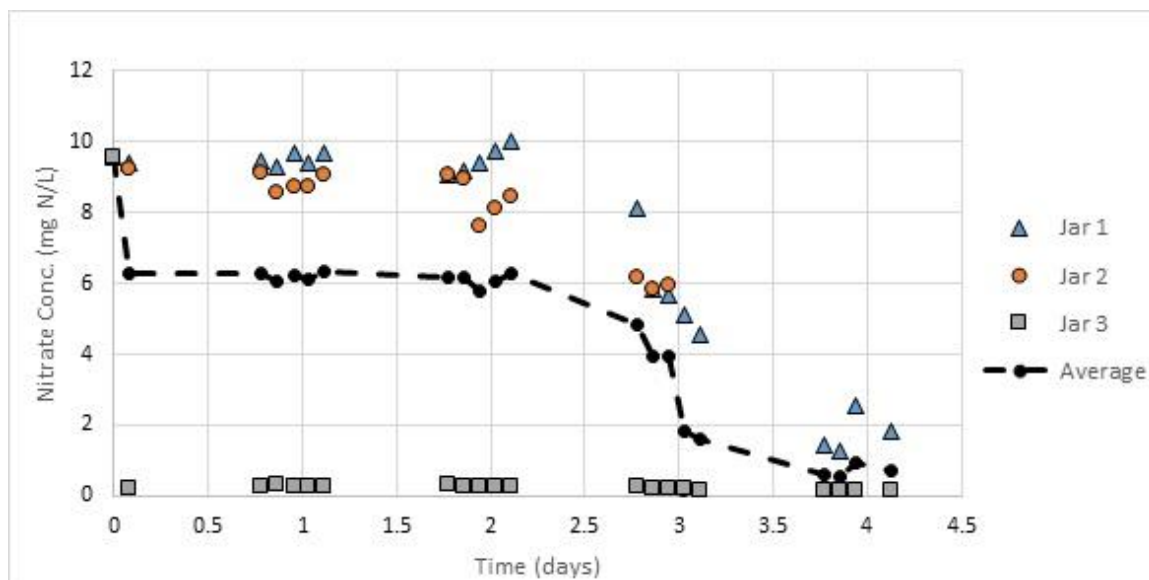


Figure C.3: Nitrate concentrations of the sterilized wood-chip replicates and the average of the replicates.

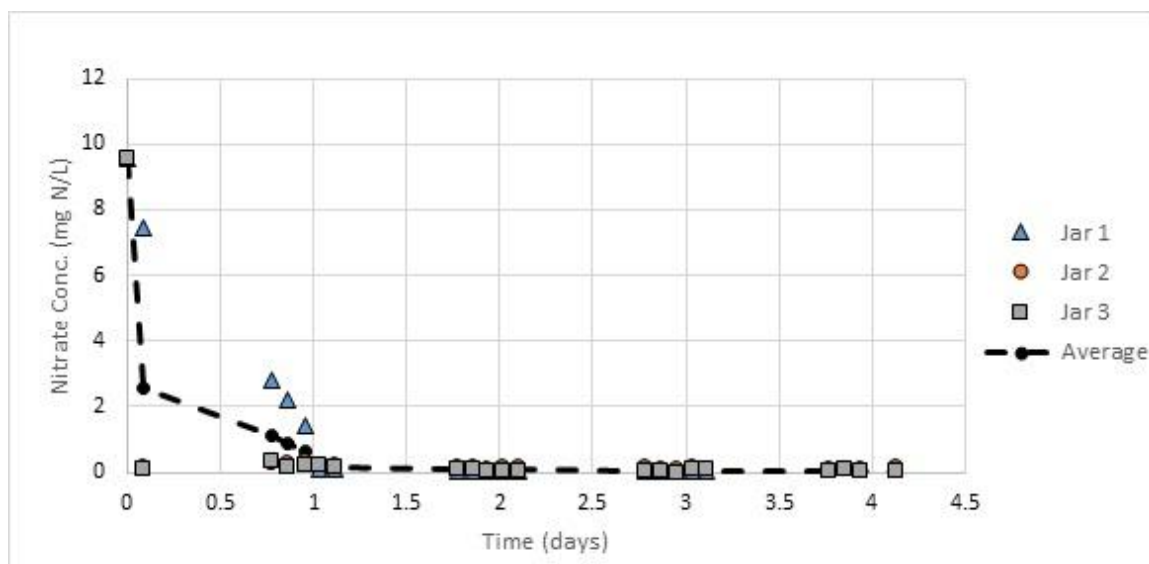


Figure C.4: Nitrate concentrations of the non-sterilized wood-chip replicates and the average of the replicates.

## Appendix D Varying pH Bauxite Data

Table D.1: SRP concentration and mass data of a solution exposed to a Bauxite disk of pH 5. The concentration and mass data was normalized by the mass of the bauxite disk.

pH 5 Bauxite		Bauxite Mass (g): 16.672			
Time (days)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.11	0.13	1	0	0
7	0.095	0.0057	0.045	0.40	0.024
10	0.063	0.0038	0.030	0.41	0.025
13	0.019	0.0011	0.009	0.42	0.025
15	0.02	0.0012	0.0095	0.42	0.025

Table D.2: SRP concentration and mass data of a solution exposed to a Bauxite disk of pH 7. The concentration and mass data was normalized by the mass of the bauxite disk.

pH 7 Bauxite		Bauxite Mass (g): 16.929			
Time (days)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.11	0.12	1	0	0
7	0.04	0.0024	0.019	0.41	0.024
10	0.03	0.0018	0.014	0.42	0.025
13	0.04	0.0021	0.017	0.42	0.025
15	0.06	0.0034	0.027	0.42	0.025

Table D.3: SRP concentration and mass data of a solution exposed to a Bauxite disk of pH 9. The concentration and mass data was normalized by the mass of the bauxite disk.

pH 9 Bauxite		Bauxite Mass (g): 17.033			
Time (days)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.09	0.12	1	0	0
7	0.037	0.0022	0.018	0.41	0.024
10	0.067	0.0039	0.032	0.41	0.024
13	0.051	0.003	0.024	0.41	0.024
15	0.14	0.0083	0.068	0.41	0.024

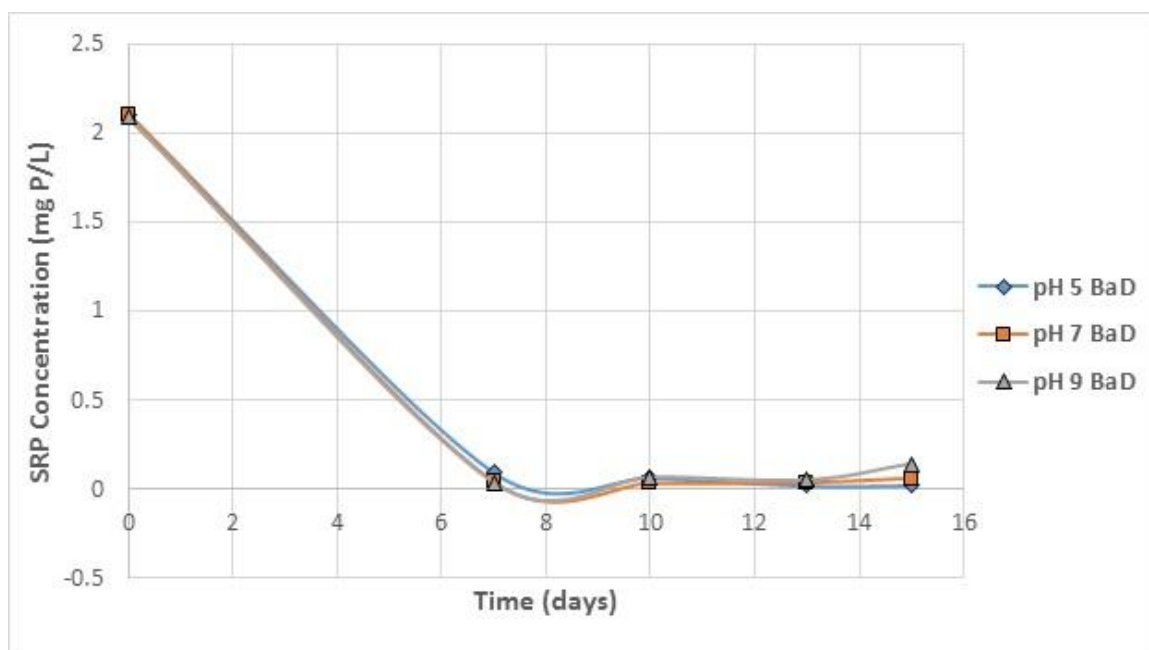


Figure D.1: The SRP concentrations of the bauxite disks with varying pH levels.



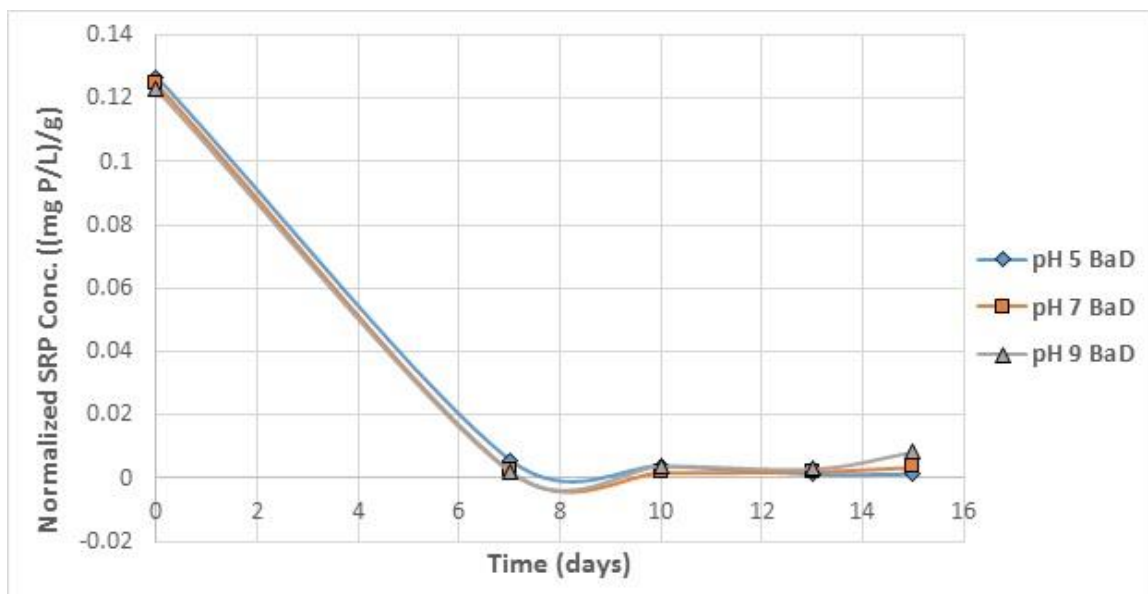


Figure D.2: The Normalized SRP concentrations of the bauxite disks with varying pH levels. To normalize, the concentrations were divided by the mass of their respective bauxite disk.

## Appendix E Varying % NaCl Bauxite Data

Table E.1: SRP concentration and mass data of a solution exposed to the NaCl Bauxite disk labeled 1. The concentration and mass data was normalized by the mass of the bauxite disk.

1 NaCl Bauxite		Bauxite Mass (g): 23.11			
Time (hours)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.24	0.097	1	0	0
1.33	1.72	0.074	0.77	0.12	0.0051
3.66	1.27	0.055	0.57	0.21	0.0092
20.66	0.30	0.013	0.14	0.40	0.017
23.08	0.35	0.015	0.16	0.40	0.017
26.08	0.53	0.023	0.24	0.40	0.017
28	0.66	0.029	0.30	0.40	0.017

Table E.2: SRP concentration and mass data of a solution exposed to the NaCl Bauxite disk labeled 3. The concentration and mass data was normalized by the mass of the bauxite disk.

3 NaCl Bauxite		Bauxite Mass (g): 21.72			
Time (hours)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.20	0.10	1	0	0
1.33	1.53	0.071	0.70	0.15	0.0070
3.66	1.14	0.052	0.52	0.24	0.011
20.66	0.64	0.029	0.29	0.33	0.015
23.08	0.51	0.023	0.23	0.35	0.016
26.08	0.49	0.023	0.22	0.36	0.016
28	0.54	0.025	0.25	0.36	0.016

Table E.3: SRP concentration and mass data of a solution exposed to the NaCl Bauxite disk labeled 5. The concentration and mass data was normalized by the mass of the bauxite disk.

5 NaCl Bauxite		Bauxite Mass (g): 19.90			
Time (hours)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)
0	2.15	0.11	1	0	0
1.33	1.35	0.068	0.63	0.18	0.0093
3.66	1.06	0.053	0.49	0.24	0.012
20.66	0.36	0.018	0.17	0.38	0.019
23.08	0.30	0.015	0.14	0.39	0.019
26.08	0.17	0.0084	0.078	0.41	0.020
28	0.19	0.0097	0.090	0.41	0.020

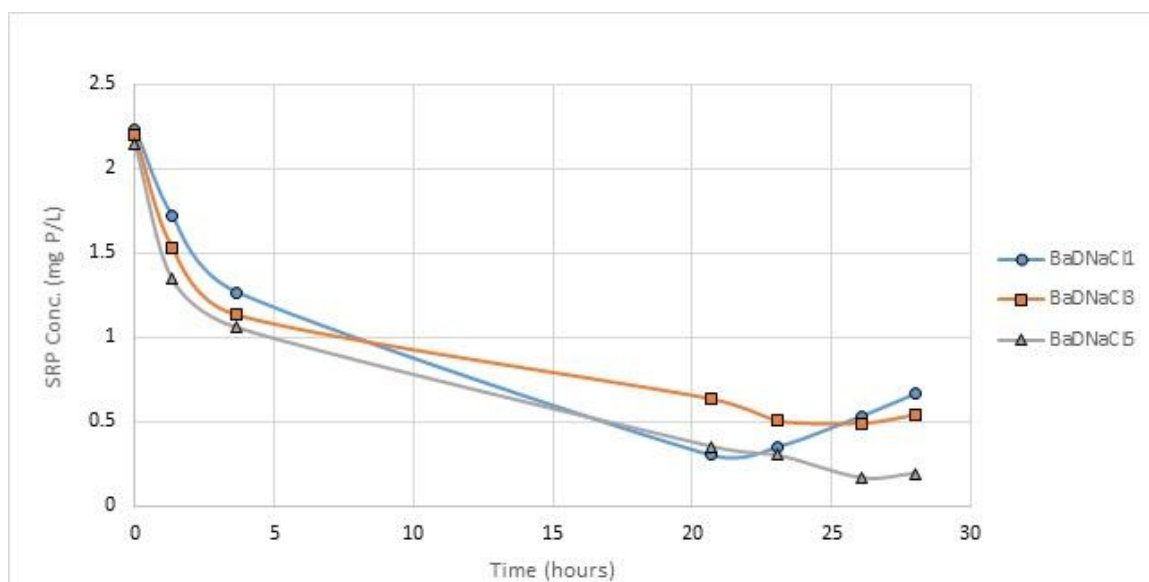


Figure E.1: The SRP concentration of the bauxite disks with varying amounts of NaCl.

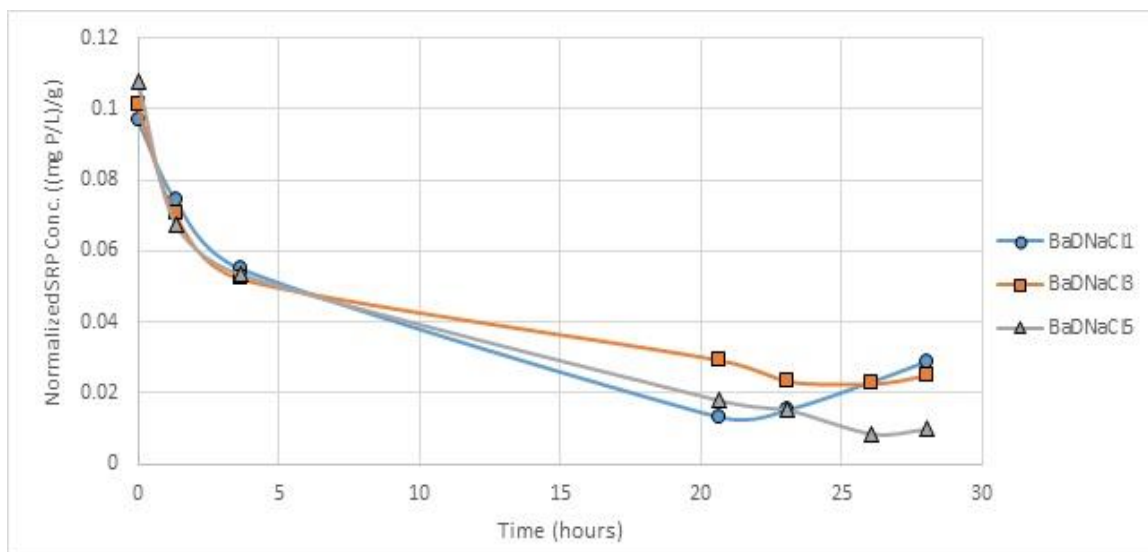


Figure E.2: The Normalized SRP concentration of the bauxite disks with varying amounts of NaCl. To normalize, the concentrations were divided by the mass of their respective bauxite disk.

## Appendix F One-hour Bauxite Test Data

Table F.1: SRP concentration and mass data of the one-hour SRP absorption test using a 3% NaCl Bauxite disk. The concentration and mass data was normalized by the mass of the bauxite disk.

3% NaCl Bauxite		Bauxite Mass (g): 21.4				
Time (min)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co	SRP in Bauxite (mg)	Normalized by Bauxite Mass (mg P/g)	
0	2.06	0.096	1.00	0.00	0.00	
2	1.58	0.074	0.76	0.24	0.011	
4	1.57	0.073	0.76	0.24	0.011	
6	1.61	0.075	0.78	0.24	0.011	
8	1.59	0.074	0.77	0.25	0.012	
10	1.57	0.073	0.76	0.26	0.012	
12	1.62	0.075	0.78	0.26	0.012	
14	1.62	0.076	0.79	0.26	0.012	
16	1.62	0.075	0.78	0.26	0.012	
18	1.61	0.075	0.78	0.26	0.012	
20	1.60	0.075	0.78	0.26	0.012	
22	1.62	0.075	0.78	0.26	0.012	
24	1.64	0.077	0.80	0.26	0.012	
26	1.60	0.075	0.78	0.28	0.013	
28	1.60	0.075	0.78	0.28	0.013	
30	1.63	0.076	0.79	0.28	0.013	
32	1.66	0.077	0.80	0.28	0.013	
34	1.61	0.075	0.78	0.29	0.013	
36	1.55	0.072	0.75	0.30	0.014	
38	1.57	0.073	0.76	0.30	0.014	
40	1.60	0.075	0.78	0.30	0.014	
42	1.54	0.072	0.75	0.31	0.015	
44	1.46	0.068	0.71	0.33	0.015	
46	1.51	0.070	0.73	0.33	0.015	
48	1.28	0.060	0.62	0.36	0.017	
50	1.56	0.073	0.76	0.36	0.017	
52	1.57	0.073	0.76	0.36	0.017	
54	1.55	0.072	0.75	0.36	0.017	
56	1.56	0.073	0.76	0.36	0.017	
58	1.51	0.070	0.73	0.37	0.017	
60	1.57	0.073	0.76	0.37	0.017	

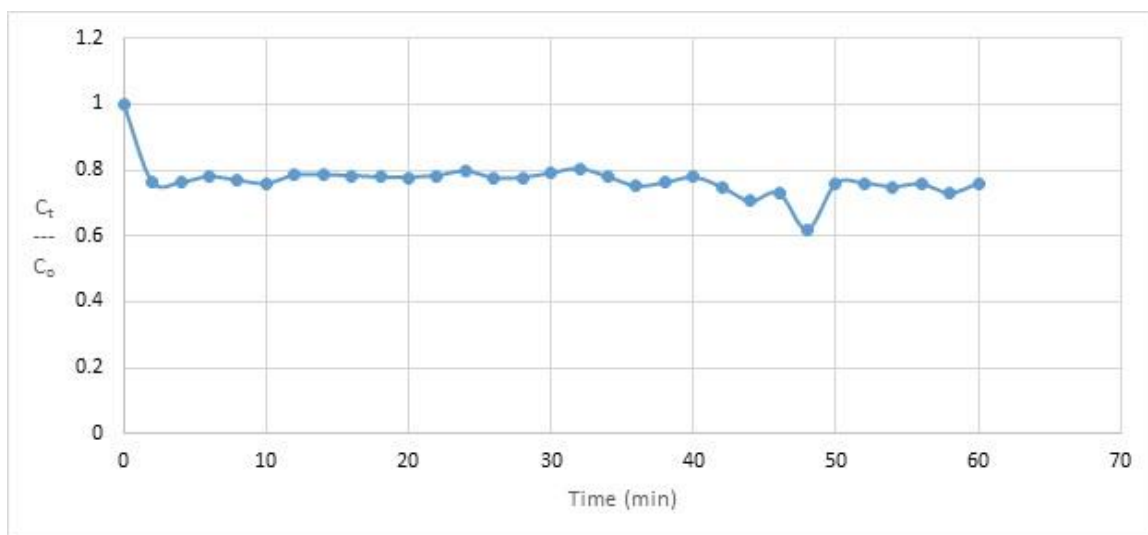


Figure F.1: The reduction in SRP concentration of the solution.

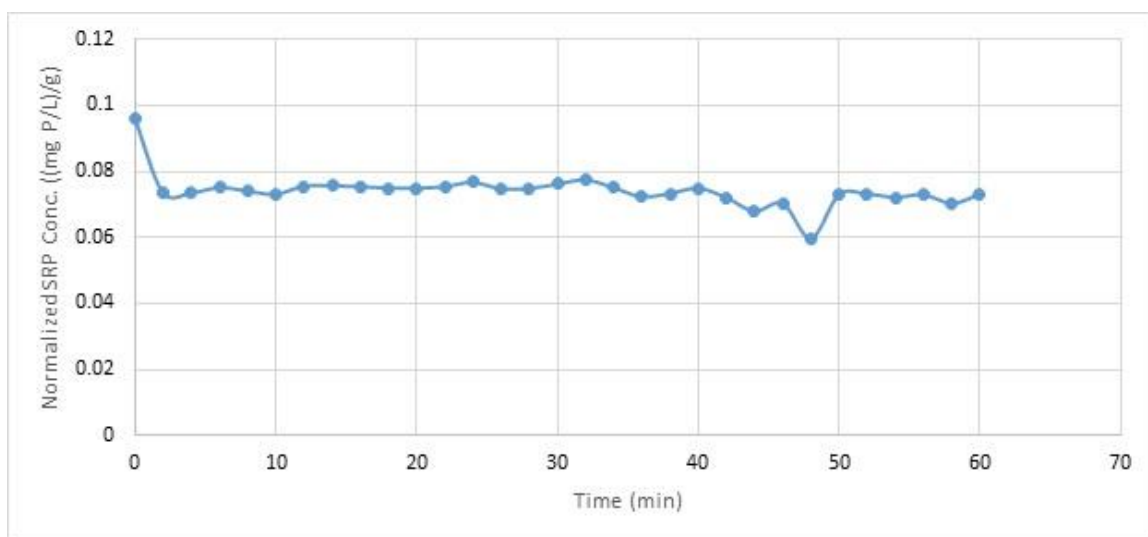


Figure F.2: The SRP concentration normalized by the mass of the bauxite disk used.

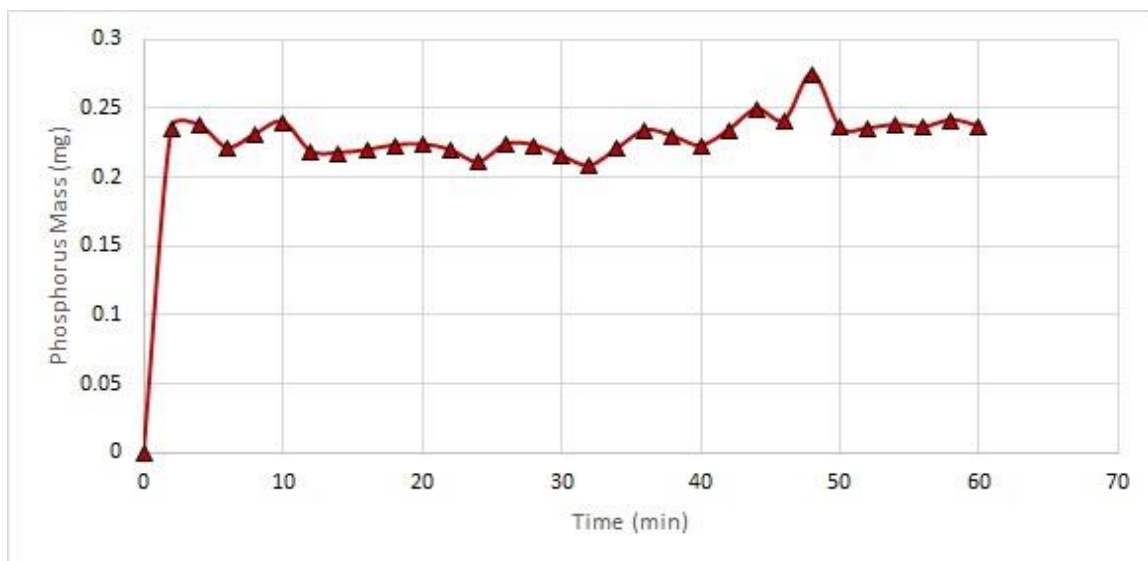


Figure F.3: Mass of phosphorus in the bauxite disk over the course of the test.

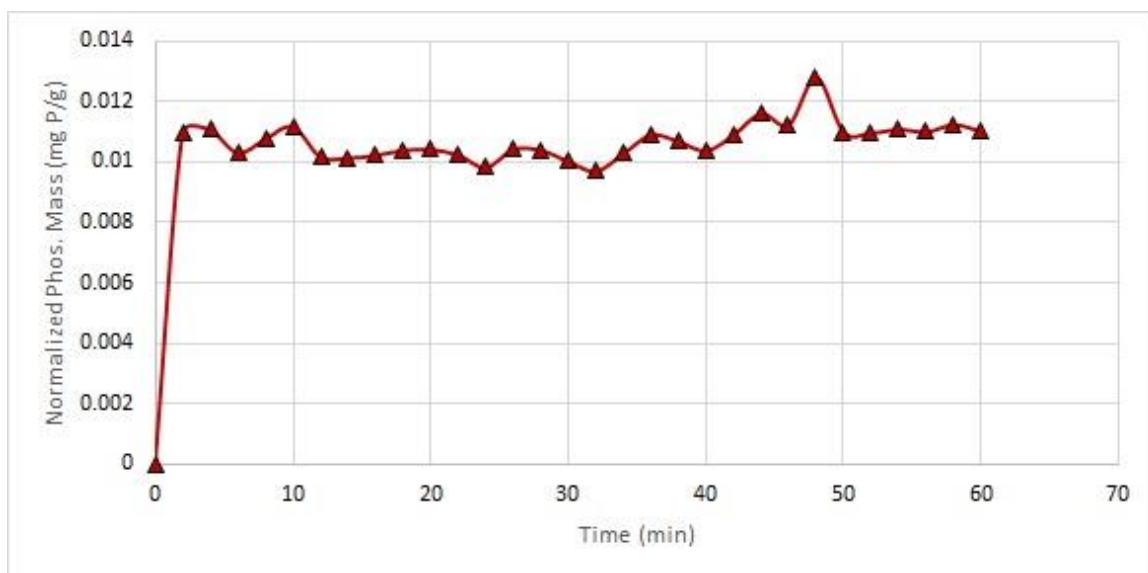


Figure F.4: Mass of phosphorus in the bauxite disk normalized by the mass of the bauxite disk.

## Appendix G Bauxite in Lab-scale Outflow Box Data

Table G.1: SRP concentration data of the lab-scale outflow box effluent using a 1% NaCl Bauxite disk. The concentration data was normalized by the mass of the bauxite disk.

1% NaCl Bauxite	Bauxite Mass (g): 22.87		
Time (min)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co
0	1.83	0.080	1.00
0.01	1.83	0.080	1.01
2	1.77	0.077	0.97
4	1.78	0.078	0.98
5	1.75	0.077	0.96
7	1.77	0.077	0.97
10	1.75	0.077	0.96
15	1.78	0.078	0.98
30	1.79	0.078	0.99
45	1.76	0.077	0.97
60	1.79	0.078	0.98
75	1.74	0.076	0.96
90	1.83	0.080	1.00
105	1.85	0.081	1.02

Table G.2: SRP concentration data of the lab-scale outflow box effluent using a 5% NaCl Bauxite disk. The concentration data was normalized by the mass of the bauxite disk.

5% NaCl Bauxite	Bauxite Mass (g): 16.83		
Time (min)	SRP Concentration (mg P/L)	Normalized by Bauxite Mass ((mg P/L)/g)	Ct/Co
0	0.45	0.027	1.00
0.01	0.44	0.026	0.98
2	0.47	0.028	1.04
4	0.47	0.028	1.04



5	0.49	0.029	1.09
7	0.53	0.031	1.18
10	0.54	0.032	1.20
15	0.45	0.027	1.00
30	0.44	0.026	0.98
45	0.44	0.026	0.98
60	0.44	0.026	0.98
75	0.44	0.026	0.98
90	0.45	0.026	1.00

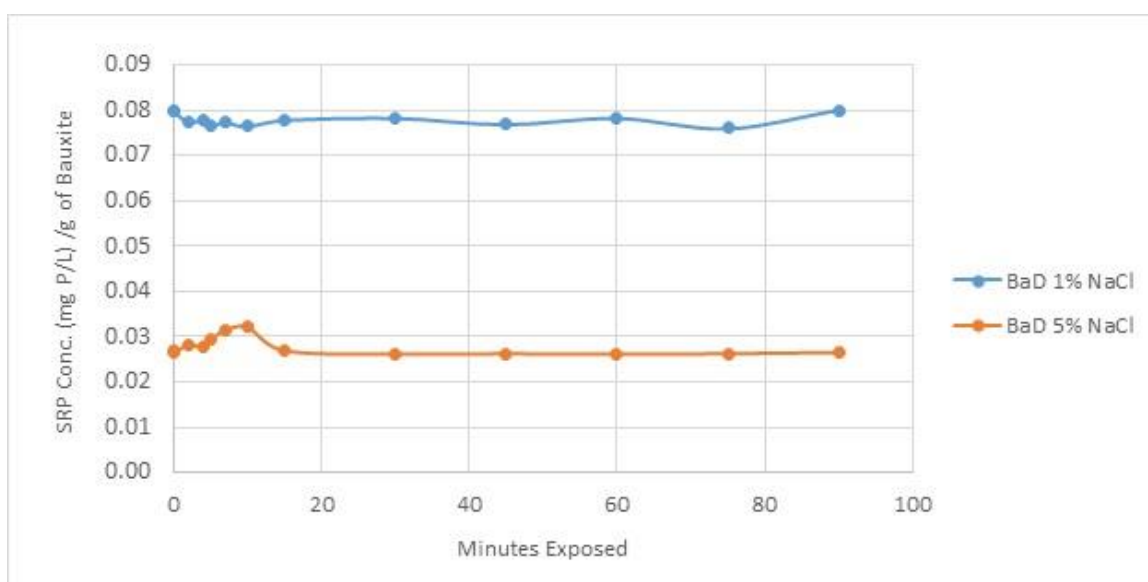


Figure G.1: The Normalized SRP concentration of the effluent from the lab-scale box for both a 1% NaCl and a 5% NaCl bauxite disk.